Synthesis and Characterization of Oxovanadium Complexes Featuring O- and N- Donor Environment

A Dissertation

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NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

Affiliated to

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CERTIFICATE

This is to certify that the thesis entitled, "***Synthesis and Characterization of Oxovanadium Complexes Featuring O- and N- Donor Environment***" submitted by Mr. Paresh Kumar Majhi in partial requirements for the award of Master of Science Degree at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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TO My PARENTS

WHO HELPED ME THROUGH OUT

AND

TO MY TEACHER

WHO TAUGHT ME THE BEAUTY OF CHEMISTRY

ACKNOWLEDGEMENTS

This thesis is the account of one year of devoted work in the field of Co-ordination Chemistry at the National Institute of Technology, Rourkela, India, which would not have been possible without the help of many.

A few lines are too short to make a complete account of my deep appreciation for my advisors Dr. Rupam Dinda. I would like to thank him with immense pleasure for his valuable guidance and constant encouragements which I have received during last two years.

I acknowledge my sincere regards to all staff's member, Department of Chemistry, NIT Rourkela for their enthusiasm in promoting the research in chemistry and for their kindness and dedication to students. I specially record my deep appreciation and thanks to Dr. Saurav Chatterjee for his indefatigable encouragements, which set me on the right track.

I would like to thank here Professor Nigam P. Rath, Research Professor, Department of Chemistry and Biochemistry, University of Missouri-St. Louis, USA, Professor Ekkehard Sinn, Professor and Chair, WMU Department of Chemistry, Kalamazoo, USA and Partha Mitra, IACS, Kolkata for single X-ray diffraction facilities.

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Date: 11. 05. 2009 Name: Paresh Kumar Majhi

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1. INTRODUCTION:

Vanadium is the only element in the periodic table that is named after a goddess (the Nordic goddess Vanadis), and perhaps with this legacy brings to the table a sense of some unpredictable and surprising chemistry. It is an early first-row transition metal and forms colorful compounds in its many different oxidation states. It undergoes a wide variety of chemistry depending on the electronic and steric nature of the coordinating ligands. In higher oxidation states, vanadium is very oxophilic, but at low oxidation states, π-donating ligands such as dinitrogen and carbon monoxide are preferred. Two decades ago, vanadium chemistry, particularly vanadium (V) chemistry, was significantly less developed than it is now. Many aspects of vanadium (V) chemistry in solution that are now well known were about to be discovered. A compendium of contributions dedicated to vanadium chemistry edited by Chasteen [1], showed the number of publications in the area of vanadium chemistry increased dramatically from the early to the late 1980s. This level of interest has continued unabated, thus leading to the much more mature field that exists presently. The barriers between bioinorganic and other areas of vanadium science are now less obvious; systems of interest to bioinorganic chemists have catalytic properties, and systems known for their catalytic properties have relevance to bioinorganic chemistry.

The catalytic and material properties of vanadium compounds and their effects in biological systems have long provided the impetus and fuel to studies of vanadium science. The expanding knowledge of the role of vanadium in biological systems and of the potential of vanadium compounds as therapeutic agents has led to a continuously increasing interest in the coordination chemistry and solution chemistry of this element. Within the spectrum of vanadium complexes that have been synthesized as model compounds for the understanding of vanadium-controlled

biological systems or as potential therapeutic agents with insulin-mimetic properties, one finds a substantial number of oxovanadium(V) chelate complexes with a variety of donor set.

Vanadium is a trace element that plays an important, perhaps essential and general role in the regulation of enzymatic phosphorylations. Several forms of life, including the fly agaric toadstool (*Amanita muscaria*) and certain sea squirts (ascidians), are able to concentrate vanadium. In other organisms vanadium is part of the active site of some enzymes. Well-studied examples are the nitrogen-fixing bacterium *Azotobacter* and various seaweeds that use vanadate-dependent peroxidases to synthesize halogenated organic compounds. Another important biological activity of vanadium is its insulin-mimetic characteristics, which can cause in vivo stimulation of the uptake and metabolism of glucose. Despite its importance as a "biometal" both in primitive, prokaryotic organisms (*Azotobacter*) and in the highly organized ascidians, which represent an early stage in the evolution of vertebrates, the bioinorganic chemistry of vanadium is still in its infancy.

The spectroscopic characterization of the oxovanadates by Howarth and coworkers [2,3] and that of alkylated oxovanadates, i.e., vanadate esters, as reported by the Gresser and Tracey team [4,5] were key studies in the area of vanadium(V) solution chemistry. The vanadium nucleus is very sensitive to small structural variations, and is a very effective tool for investigation of vanadium compounds in solution. Characterizing the molecular structure is a critical component of understanding the properties of a complex and the determination of X-ray structure remains an important endeavor in all areas of chemistry. This includes results using the tools of solid state and modeling compounds to probe the coordination chemistry of vanadium (V) complexes.

The rich chemistry of vanadium in the +V oxidation state in comparison to other two biologically important states, e.g. +IV and +III, is probably due to its ability to exist in three

forms, viz., VO^{3+}, VO_2^+ and $V_2O_3^+$. In vanadium chemistry, the VO^{2+} and VO^{3+} motifs have received considerable attention probably due to their involvement in many vanadium-dependent enzymes, viz., nitrogenases [6], haloperoxidases [7], phosphomutases etc. Catalytic activity of some vanadium(V) complexes in a-olefin polymerization has recently been discovered [8]. Moreover, the discoveries of several medicinal properties of vanadium complexes viz., insulin-mimetic, anticancer, antitumour and antifungal/antibacterial activities [9, 10] have stimulated further research in this area. In most cases the active site contains either of these two motifs coordinated by oxygen–nitrogen atoms. The strong affinity of these two motifs towards O, N-donor ligand is probably due to their hard acidic nature and selective stabilization of these two motifs depends upon the basicity of donor atoms. These ligands have a tendency to stabilize the vanadium in its highest oxidation state [11-13]. Electronic property of the metal ion in a complex can be tuned by changing the coordination environment around the metal ion and this can be done by two ways in a mixed-ligand system: (i) by making substitution on either or both of the coordinated ligands and (ii) by changing one ligand with varying basicity.

A recent report [14] reveals the structure of an azide derivative of the chloroperoxidase from the fungus *Cur*V*ularia inæqualis*, wherein the vanadium(V) center is bound to three oxygen donors and an azide, while a histidine imidazole acts as the sole protein-derived ligand. The involvement of vanadoenzymes in both reductive ($N_2 + 6H^+ + 6e \rightarrow 2NH_3$) and oxidative ($RH + H_2O_2 + HX \rightarrow RX + 2H_2O$) transformations signifies the importance of the +3, +4, and +5 oxidation states. The synthesis as well as characterization of low molecular weight complexes with these biologically important oxidation states of vanadium will help in making further progress in the elucidation of the biological roles of vanadium. Vanadium easily switches between the oxidation states IV and V and the stabilization of either of these two states under aerobic condition depends upon the

basicity of the coordinated ligand and also on the pH of the reaction medium. Of these three, the +V state has received considerable attention probably due to its two important properties: (i) it can exist in three motifs viz., mononuclear VO^{3+} and VO_2^{+} motifs and dinuclear $V_2O_3^{4+}$ motif and (ii) it has the ability to exist in either five or six coordinated environment. These motifs are stable in solution around the physiological pH (~7) only when the metal is coordinated with sufficiently strong ligand for preventing the precipitation of hydroxides. A systematic study regarding the exclusive formation of any one of these three motifs with O, N-donor ligands [as V (V) due to its hard acidic nature, has strong affinity towards hard basic O, N-donor ligands] and their interconversion is an important area of contemporary research. Hydrazone ligands derived from the condensation of acid hydrazide with aromatic carbonyl compounds are important tridentate O, N-donor ligands containing two intermediate basic phenolic and amide groups and one neutral imine moiety. This type of work was motivated by four objectives: (i) to synthesize the complexes containing $V_2O_3^{4+}$ core with a family of above mentioned hydrazone ligands, (ii) to rationalize the various synthetic routes for the formation of such type of complexes with these hydrazone ligands, (iii) to examine the feasibility of conversion of these dinuclear complexes into the mononuclear complexes with VO^{3+} and VO_2^{+} motifs.

Interest in the coordination chemistry with particular emphasis on the model character of vanadium(V) complexes having O and N functionalities stems from the structural characterization of three vanadate-dependent haloperoxidases (VHPO). Irrespective of their origin from brown algae (*Ascophyllum nodosum*) [15], red algae (*Corallinaofficinalis*), or fungi *(Cur*V*ularia inequalis*) [16], they all show a high degree of amino acid homology in their active centers and have almost identical structural features, with vanadium(V) in a trigonal-bipyramidal coordination environment. Vanadium is covalently linked to three nonprotein oxo groups in the

equatorial plane, to the protein backbone through N_e of an imidazole moiety of a proximal histidine, and to an axial OH group trans to the histidine, further hydrogen bonded to a distal (catalytic) histidine and water molecules. These enzymes, as well as various model complexes, catalyze the oxidation, by peroxide, of halide to hypohalous acid [16, 17] and of (prochiral) sulfides to (chiral) sulfoxides, and of several other organic substrates.

The coordination chemistry of aroyl hydrazones are quite interesting as it presents a combination of donor sites such as protonated / deprotonated amide oxygen, an imine nitrogen of hydrazone moiety and additional donor site (usually N or O) provided from the aldehyde or ketone forming the Schiff base.

$[VO(acac)_2]$ serves as a good precursor and undergoes ligand exchange reaction where one or both acetylacetonato groups can easily be exchanged with organic ligands having coordinating atoms of different potentialities. Usually oxovanadium (IV) complexes form when $[VO(acac)_2]$ reacts with ligands under anhydrous conditions. Under aerobic conditions most vanadium complexes stabilize in their highest oxidation state (i.e. V). Factors such as nature of ligands, solvents, pH of the reaction and reaction medium etc. have, however, great influence on the stoichiometry and nature of the resulting complexes.

In this dissertation I report the synthesis, structure and full characterization of a new mononuclear square pyramidal monoalkoxo-bound monooxo-vanadium (V) complex $VOL_2^S(OEt)$ (**1**) of *2*-Hydroxyacetophenonehydrazone of *2*-Hydroxybenzoylhydrazine Ligand. I also report the synthesis of several other Schiff's base ligands and their respective oxovanadium complexes. But due to insufficient data and shortage of time we are unable to report the complete characterization of all other complexes (**2-4**).

2. EXPERIMENTAL:

2.1. Physical Measurements:

Elemental analyses (C, H, and N) were performed by Perkin-Elmer 240 instrument. FTIR spectra (4000-400 cm^{-1}) as KBr discs of the samples were recorded on a Perkin Elmer spectrum RXI. Electronic spectra were obtained using a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. Magnetic susceptibility was measured with a Sherwood Scientific MSBMK1 sample magnetometer with Hg [$Co(SCN)_4$] as calibrant. Electrochemical measurements were made at 298 K under a dry nitrogen atmosphere using a PC-controlled EG & G/PAR-273A potentiostat. A conventional three electrode configuration was used, consisting of platinum-wire working and auxiliary electrodes and an SCE reference electrode and TEAP as the supporting electrolyte. The ferrocene/ferrocenium (Fe/Fe^{+}) couple was used as the internal standard.

2.2. Chemicals and Solvents:

Chemicals were procured from renowned companies like Aldrich, E. Merck and Fluka and used without further purification. HPLC grade acetonitrile, dichloromethane and chloroform were used for spectroscopic studies. All other solvents were A.R. grade and used as received for synthetic work. NH_4VO_3 and $VOSO_4$ were procured from Loba Chemie. [$VO(acac)_2$] was prepared as described in the literature [17, 25].

2.3. Synthesis of the Ligands:

The synthesis of our final ligand consists of two steps.

Step-1: Synthesis of acid hydrazide

The two acid hydrazides were prepared by known [13, 25] methods which are schematically shown below:

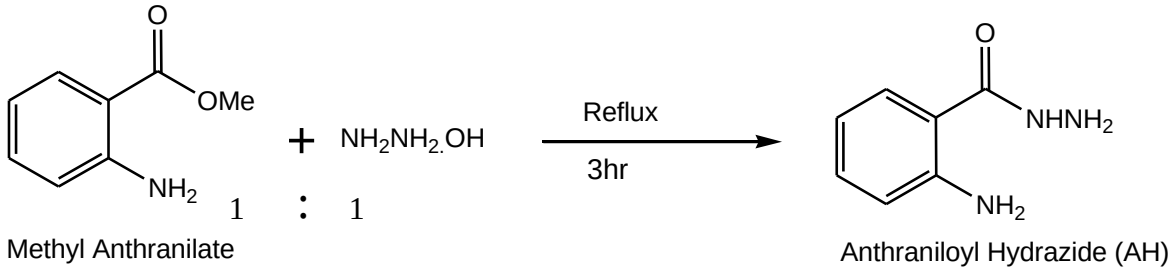


Figure 1.1

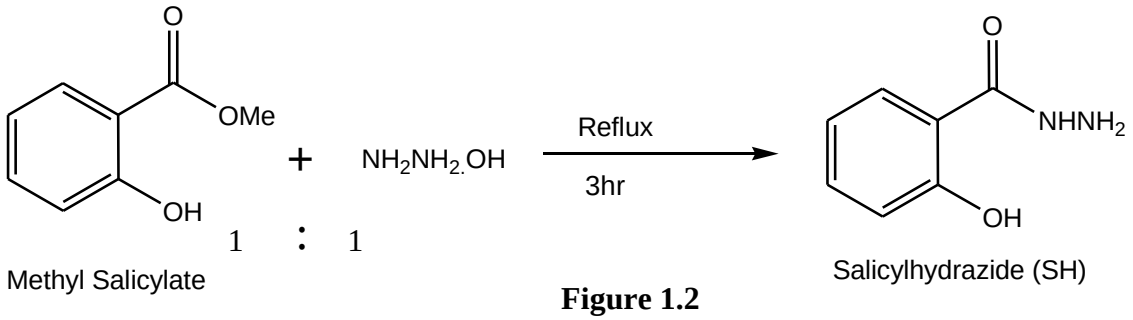
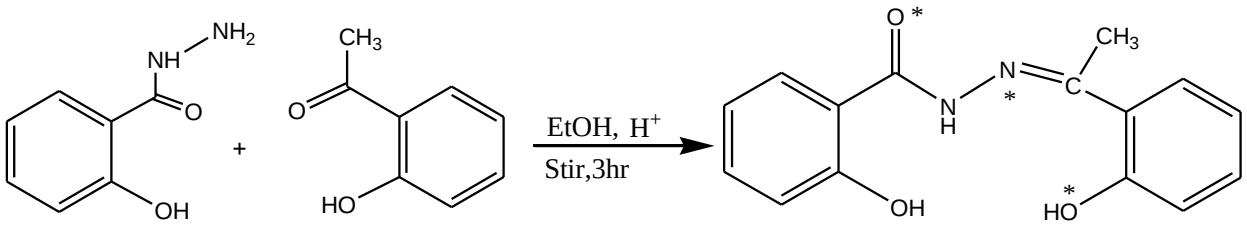


Figure 1.2

Step-2: Synthesis of Schiff's base ligand

All the four Schiff's base ligands used in this study were prepared following same method by stirring carbonyl compounds and the respective hydrazide in equimolar ratio. A typical synthesis is described below.

A. *2*-Hydroxyacetophenonehydrazone of *2*-Hydroxybenzoylhydrazine Ligand, **($L_2{}^SH_2$)**



1 : 1

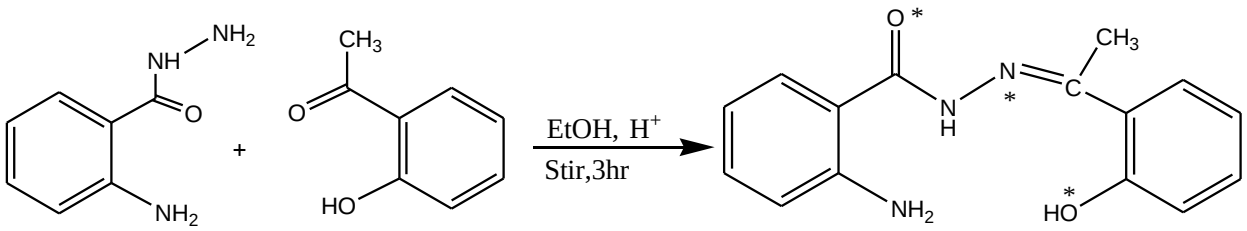
Salicylhydrazide 2-hydroxyacetophenone Ligand ($L_2{}^SH_2$)

Figure 2.1

Schiff base ligand, *2*-hydroxyacetophenonehydrazone of *2*-hydroxybenzoylhydrazine ($L_2{}^SH_2$) was prepared by reacting salicylhydrazide (1.52-g / 10-mmol) and *2*-hydroxy acetophenone (1.36-g / 10-mmol) in stirring ethanol (25 mL) for 3 h. The resulting white compound was filtered and washed three times with ethanol and dried over fused $CaCl_2$.

M.P.170^{o}C. Yield: 70%. Found (Calc. for $C_{15}H_{13}N_2O_3$): C 66.71 (66.66), H 4.85 (4.81), N 10.38 (10.37). Selected IR bands (cm^{-1}): 3268 (ν_{O-H}), 1629 ($\nu_{C=O}$), 1581 ($\nu_{C=N}$), 3056 (ν_{N-H}).

B. *2*-Hydroxyacetophenonehydrazone of *2*-Aminobenzoylhydrazine Ligand, **($L_2{}^AH_2$)**



1 : 1

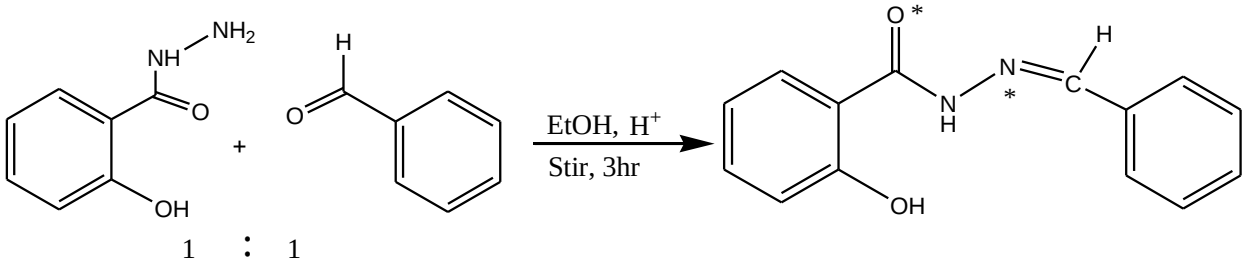
Anthranilhydrazide 2-hydroxyacetophenone Ligand ($L_2{}^AH_2$)

Figure 2.2

It was prepared by a similar method to that of $L_2{}^SH_2$ **(A)** above using anthranilhydrazide and *2*-hydroxyacetophenone. M.P.160^{o}C. Yield: 71%. Found (Calc. for $C_{15}H_{15}N_3O_2$): C 66.95 (66.91),

H 5.57 (5.59), N 15.64 (15.61). Selected IR bands (cm^{-1}): 3476 (ν_{N-H2}), 1627 ($\nu_{C=O}$), 1573 ($\nu_{C=N}$), 3364 (ν_{N-H}).

C. Benzaldehydehydrazone of *2*-Hydroxybenzoylhydrazine Ligand, **($L_1{}^SH_1$)**



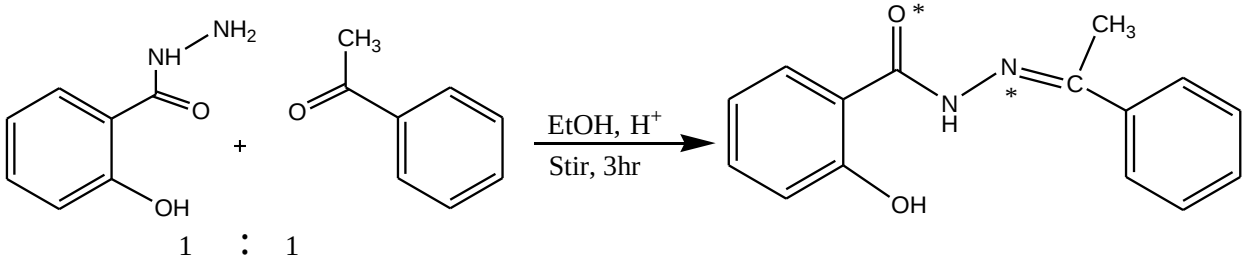
1 : 1

Salicylhydrazide Benzaldehyde Ligand ($L_1{}^SH_1$)

Figure 2.3

It was prepared by a similar method to that of $L_2{}^SH_2$ **(A)** above using salicylhydrazide and benzaldehyde. M.P.175°C. Yield 72%. Found (Calc. for $C_{14}H_{12}N_2O_2$): C 70.08 (70.00), H 5.05 (5.00), N 11.68 (11.66). Selected IR bands (cm^{-1}): 3240 (ν_{O-H}), 1629 ($\nu_{C=O}$), 1560 ($\nu_{C=N}$), 3027 (ν_{N-H}).

D. Acetophenonehydrazone of *2*-Hydroxybenzoylhydrazine Ligand, **($L_2{}^SH_1$)**



1 : 1

Salicylhydrazide Acetophenone Ligand ($L_2{}^SH_1$)

Figure 2.4

It was prepared by a similar method to that of $L_2{}^SH_2$ **(A)** above using salicylhydrazide and acetophenone. M.P.175^o C. Yield 75%. Found (Calc. for $C_{15}H_{14}N_2O_2$): C 70.88 (70.86), H 5.55 (5.51), N 11.08 (11.02). Selected IR bands (cm^{-1}): 3276 (ν_{O-H}), 1638 ($\nu_{C=O}$), 1606 ($\nu_{C=N}$), 3053 (ν_{N-H}).

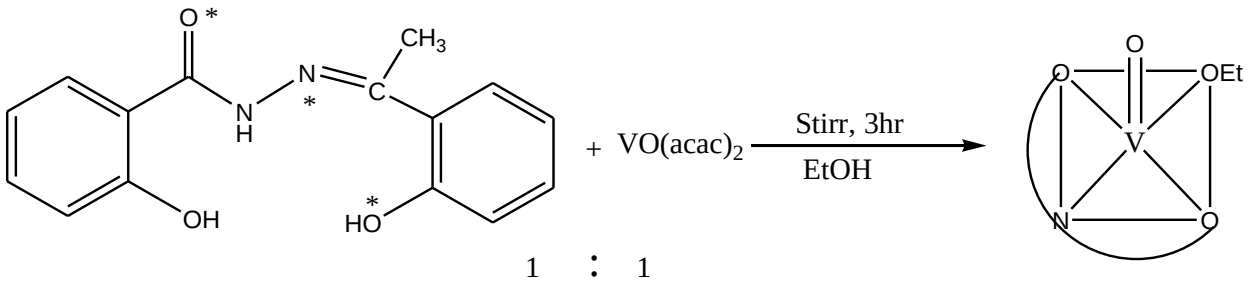
2.4. Synthesis of the Metal complexes:

A. Complex 1, $[V^VOL_2{}^S(OEt)]$:

The complex **1** can be synthesized by following two methodologies starting from two different metallic precursors.

Method – 1:

A 0.27-g (1.00-mmol) sample of ligand $L_2{}^SH_2$ was dissolved in 30 mL of ethanol and 0.265-g (1.00-mmol) of vanadium (IV) acetylacetonate was added to the stirring solution. Color of the solution slowly changed to dark brown. After 3 h of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 3 days produced dark brown crystals. Crystal structure determination is under progress.



1 : 1

Ligand ($L_2{}^SH_2$)

Figure 3.1

$V^VOL_2{}^S(OEt)$

Yield: 70%. Found (Calc. for $C_{17}H_{17}N_2O_5V$): C 53.54 (53.52), H 4.72 (4.75), N 7.34 (7.36). Selected IR bands (cm^{-1}): 3570 (ν_{O-H}), 1252 (ν_{C-O}), 1623 ($\nu_{C=N}$), 1595 ($\nu_{C=N}$). Electronic spectrum in $CHCl_3$ solution, λ nm (ε M^{-1} cm^{-1}): 403 (3928), 368 (5400), 358 (5497).

Method – 2:

A 0.27-g (1.00-mmol) sample of ligand $L_2{}^SH_2$ was dissolved in 30 mL of ethanol and 0.117-g (1.00-mmol) of NH_4VO_3 was added to the stirring solution. Color of the solution slowly changed to yellow. After 3 h of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 4 days produced needle shaped crystals. We have solved the crystal structure also.

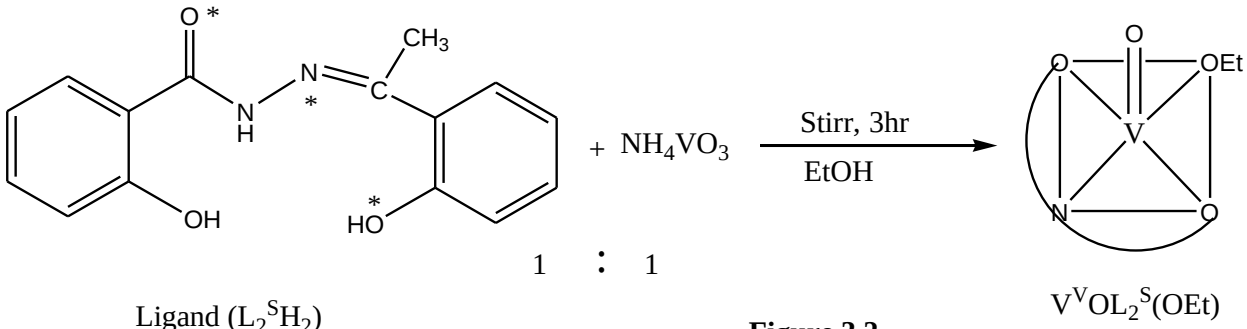
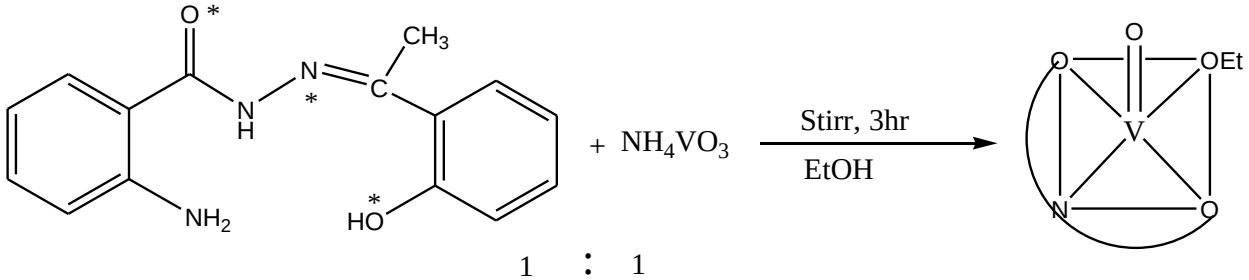


Figure 3.2

Yield~65%. Found (Calc. for $C_{17}H_{17}N_2O_5V$): C 53.54 (53.52), H 4.72 (4.75), N 7.34 (7.36). Selected IR bands (cm^{-1}): 3551 (ν_{O-H}), 1250 (ν_{C-O}), 1620 ($\nu_{C=N}$), 1598 ($\nu_{C=N}$).

B. Complex 2**,** $[V^VOL_2{}^A(OEt)]$:

A 0.269-g (1.00-mmol) sample of ligand $L_2{}^AH_2$ was dissolved in 30 mL of ethanol and 0.117-g (1.00-mmol) of NH_4VO_3 was added to the stirring solution. Color of the solution slowly changed to yellow. After 3 h of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 6 days produced brown crystals.



Ligand ($L_2^AH_2$)

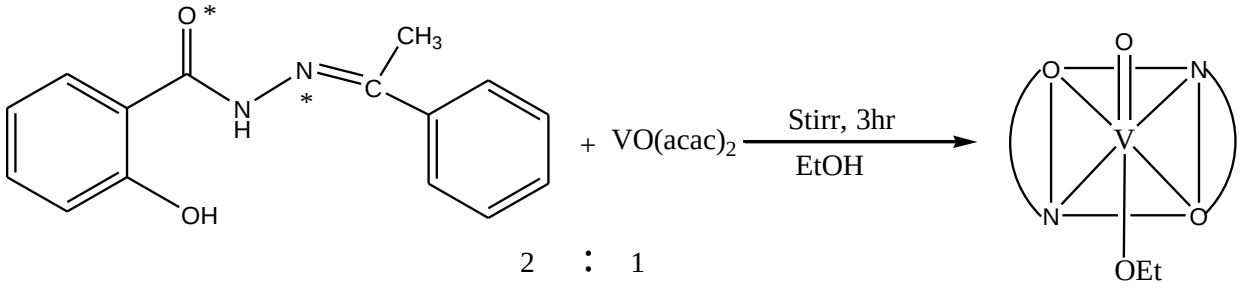
$V^VOL_2^A(OEt)$

Figure 3.3

Yield: 60%. Found (Calc. for $C_{17}H_{18}N_3O_4V$): C 53.82 (53.87), H 4.74 (4.72), N 11.08 (11.10). Selected IR bands (cm^{-1}): 3160 (ν_{N-H_2}), 1255 (ν_{C-O}), 1615 ($\nu_{C=N}$), 1596 ($\nu_{C=N}$). Electronic spectrum in $CHCl_3$ solution, λ nm (ε M^{-1} cm^{-1}): 431 (4590), 374 (5377), 358 (5460), 317 (6378).

C. Complex **3,** $[V^VO(L_2^S)_2(OEt)]$:

A 0.254-g (1.00-mmol) sample of ligand $L_2^SH_1$ was dissolved in 30 mL of ethanol and 0.133-g (0.5-mmol) of vanadium (IV) acetylacetonate was added to the stirring solution. Color of the solution slowly changed to yellow. After 3 h of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 4 days produced needle shaped crystals. Crystal structure determination is under progress.



Ligand ($L_2^SH_1$)

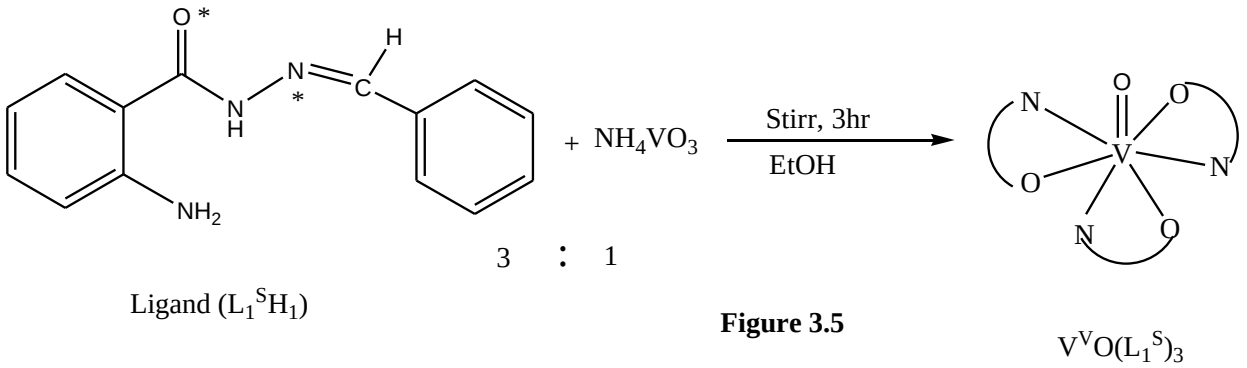
Figure 3.4

$V^VO(L_2^S)_2(OEt)$

Yield: 65%. Found (Calc. for $C_{32}H_{31}N_4O_6V$): C 62.33 (62.38), H 5.03 (5.10), N 9.09 (9.11). Selected IR bands (cm^{-1}): 3059 (ν_{O-H}), 1255 (ν_{C-O}), 1625 ($\nu_{C=N}$), 1598 ($\nu_{C=N}$).

D. Complex **4**, $[V^{V}O(L_1{}^{S})_3]$:

A 0.254-g (1.00-mmol) sample of ligand $L_1{}^{S}H_1$ was dissolved in 30 mL of ethanol and 0.039-g (0.33-mmol) of NH_4VO_3 was added to the stirring solution. Color of the solution slowly changed to yellow. After 3 h of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 3 days produced rhombic shaped crystals. Crystal structure determination is under progress.



Ligand ($L_1{}^{S}H_1$)

Figure 3.5

$V^{V}O(L_1{}^{S})_3$

Yield: 60%. Found (Calc. for $C_{42}H_{33}N_6O_4V$): C 64.28 (64.34), H 4.20 (4.25), N 10.70 (7.64). Selected IR bands (cm^{-1}): 3240 (ν_{N-H2}), 1235 (ν_{C-O}), 1630 ($\nu_{C=N}$), 1563 ($\nu_{C=N}$). Electronic spectrum in $CHCl_3$ solution, λ nm (ε M^{-1} cm^{-1}): 343 (10140), 324 (10956), 310 (10991).

2.5. X-Ray Structure Determination:

Single crystals of **1** were obtained by slow evaporation of ethyl alcohol solution of the complex. A deep yellow needle shaped crystal of **1** was chosen for X-ray diffraction study. Crystal data and details of refinement for the complex $VOL_2{}^{S}(OEt)$ are given in **Table 1.2**. The compound crystallized in the monoclinic space group $P2_1/c$. Intensity data were collected at 100 K on a

Bruker Smart CCD area detector system using graphite- monochromatised Mo-Kα radiation (λ = 0.71073 Å). The intensities were corrected for empirical absorption effects using SADABS [18]. The structure was solved by direct method. All non-hydrogen atoms were refined anisotropically by full-matrix least squares, with a riding model for the hydrogen atoms, using the SHELXTL package [19].

2.6. Magnetic Susceptibility Measurement:

Magnetic susceptibility value can be calculated by the given equation:

$\chi_g = C \times L(R - R°)/10^9 \times M$

C = Constant =1

l = length of the tube

M =Mass of the sample

R^0 =Reading for empty tube

R=Reading for sample with tube

$\chi_g = [C \times L(R - R°)/10^9]\, 10^6$

Molecular weight of metal complex = 380

Wt. of the sample (M) = 0.0307 gm

R^0= -030

l = 1.75 cm

R = -034

χ_g = 1× 1.5(-034+ 030) ÷ (10^9 × 0.0307)

= 1× 1.5 (-4) ÷ (10^9 × 0.0307)

= - 6 ÷ (10^9 × 0.0307)

$= - 195.43 \times 10^{-9}$

$= - 1.95 \times 10^{-7}$

$\chi_g \times 10^6 = - 1.95 \times 10^{-7} \times 10^6$

$= - 0.19$

$\chi_m = \chi_g \times 10^{-6} \times$ molecular wt. of complex

$= - 0.19 \times 10^{-6} \times 380$

$= - 72.2 \times 10^{-6}$

$\mu_{eff} = 2.84 \sqrt{\chi_m T}$

$= - 2.84 \sqrt{(72.2 \times 10^{-6})} \times 314$

$= - 2.84 \times 8.49 \times 10^{-3} \times 314$

$\mu_{eff} = - 7.65$ (Observed Value)

Negative value i.e. Diamagnetic

3. RESULTS AND DISCUSSION:

3.1. Protonated / Deprotonated form of Schiff's Base:

All the tridentate ligands used in this work have two possible sites of deprotonation. The tridentate Schiff's base ligands **Figure 3.6** can undergo deprotonation from enolised amide oxygen as well as from the phenolic oxygen. The bidentate Schiff's bases can undergo deprotonation from only enolised amide oxygen.

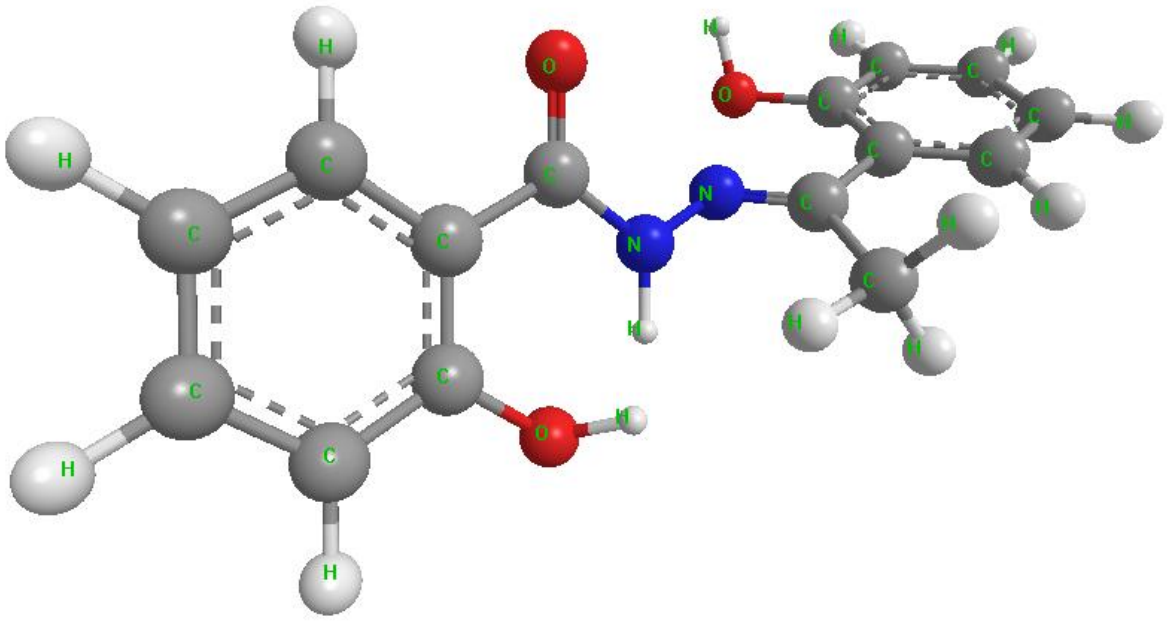
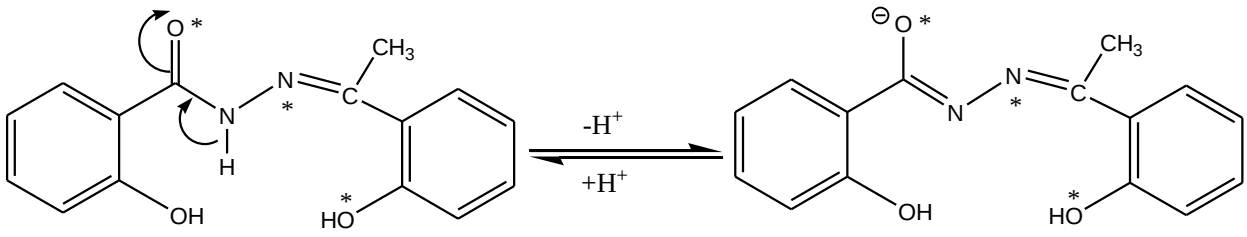


Figure 3.6 Calculated Ball & Stick model of Ligand, $\mathbf{L_2{}^SH_2}$

When the Schiff's base ligands are reacted with a V(IV) salt, the ligands **Figure 4.1** get deprotonated from the enolised amide oxygen as well as from the phenolic oxygen and the V(V) complex is obtained due to aerial oxidation of the V(IV). This is supported by the disappearance of the $\nu_{C=O}$ band in the 1630-1675 cm^{-1} region, and appearance of two $\nu_{C=N}$ band in the 1620-

1550 cm^{-1} region [13, 25]. When they reacted with V(V), the ligands behaves same to that of V(IV). So in both cases we get vanadium (V) complex.



Keto form **Figure 4.1** Enol form

2.3. ***Spectral characteristics***

A. **IR** Spectra

IR spectra of the ligand **Figure 4.2** has several prominent bands at 3268, 3056 and 1628 cm^{-1} due to ν(OH), ν(NH) and ν(C=O) stretching modes respectively, all of which are missing in the IR spectra of complex **1 Figure 4.3**. Characteristics strong bands in the spectra of both the ligand and the complex **1** are located at 1625 cm^{-1} and 1558 cm^{-1} which arise due to ν(C=N) and ν(C=C/aromatic) stretching modes of the ligand. In addition, each of the complex exhibits a strong band in the 950-999 cm^{-1} region which is attributed to the V=O stretching mode. A new band at 863cm^{-1} is located in the spectrum of the complex in solution ($CHCl_3$), which is assigned to asymmetric V-O-V bridge vibration [13, 25].

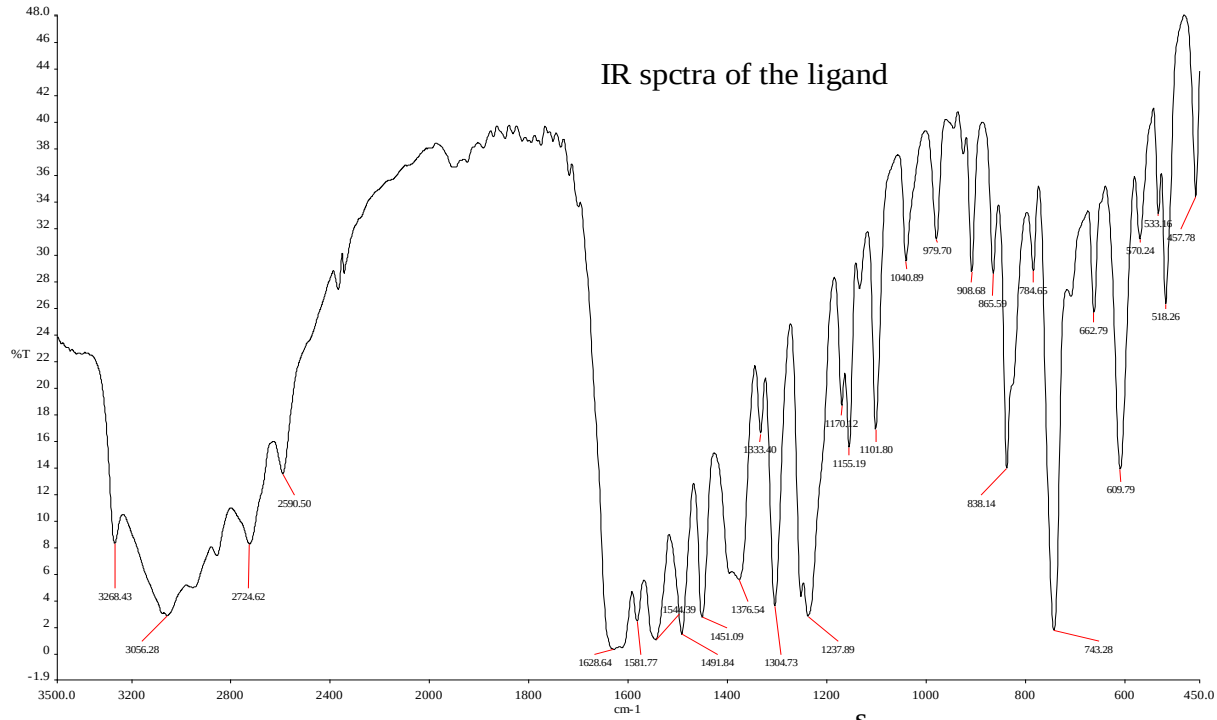


Figure 4.2 IR spectra of the ligand, $\mathbf{L_2{}^SH_2}$

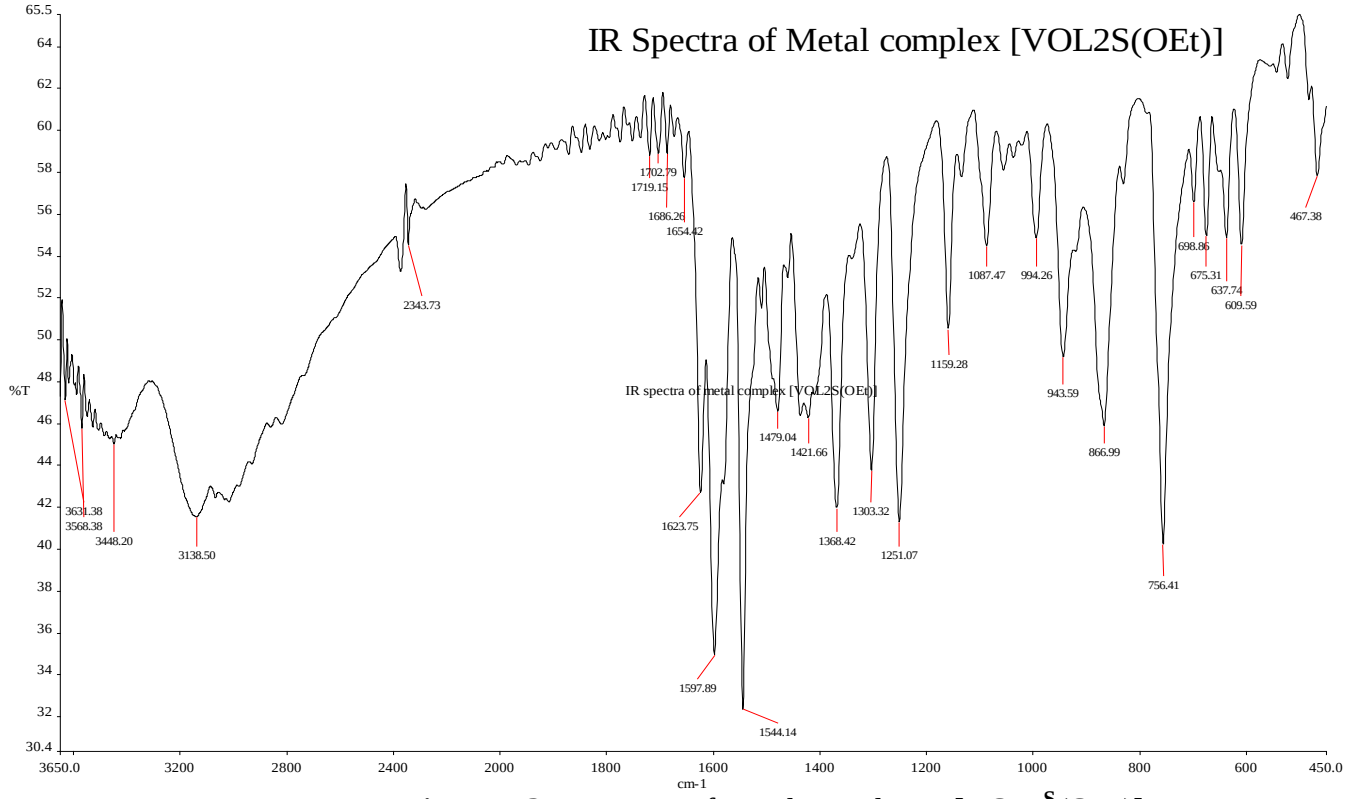


Figure 4.3 IR spectra of metal complex **1, [$\mathbf{VOL_2{}^S(OEt)}$]**

IR Spectra of Complex **1** in Solution: Identification of the minor species:

When IR spectrum of complex **1** (KBr disc) is recorded **Figure 4.4a**, one strong, sharp ν(V=O) band at 1000 cm^{-1} pointed to its monomeric nature. But when IR spectrum of **1** is recorded in $CHCl_3$ solution **Figure 4.4b** two new ν(V=O) bands appear at 1035 cm^{-1} and 1028 cm^{-1} and another new band corresponding to the ν(V-O-V) mode is located at 890 cm^{-1}. This band was absent in the spectrum of **1** in the solid state and is diagnostic of a μ-oxo dimeric V(V) species [13].

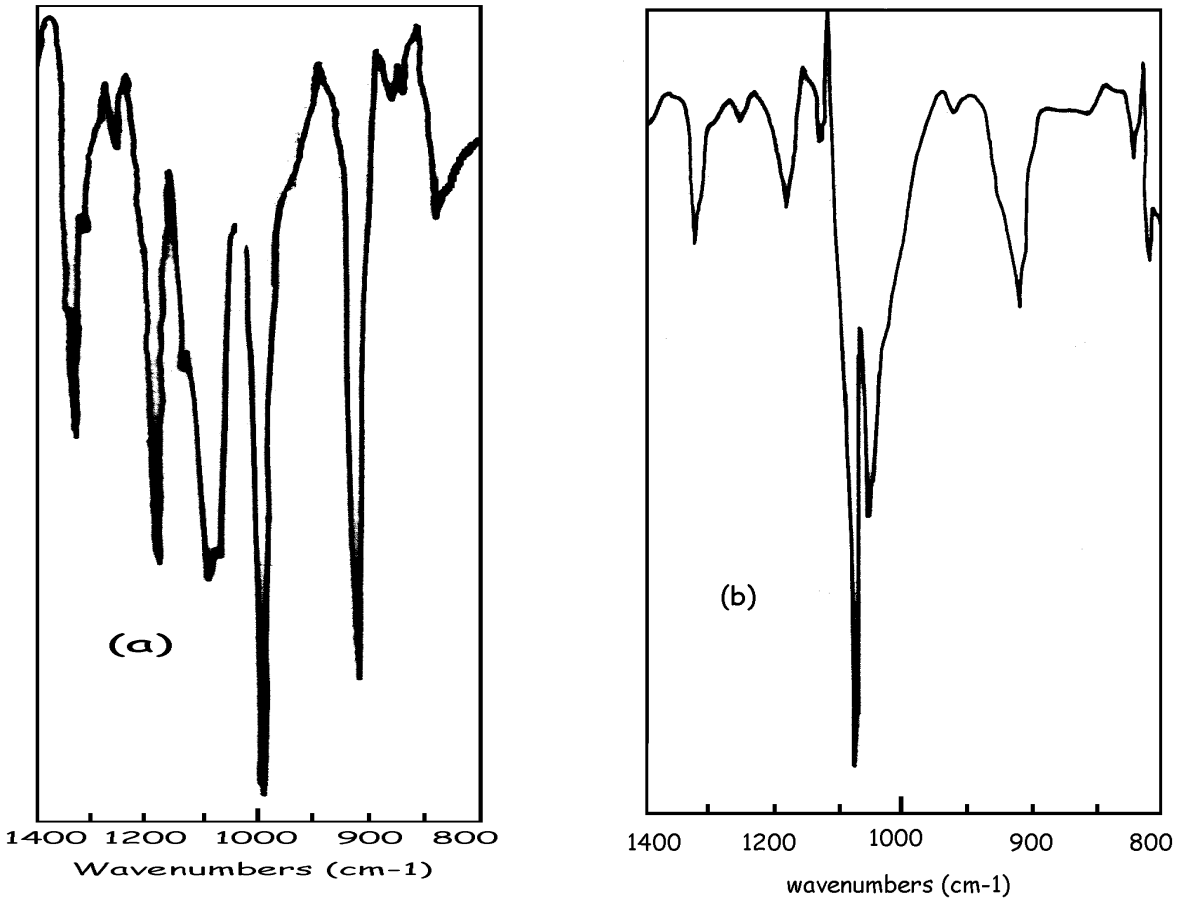


Figure 4.4 IR spectrum of **1, VOL_2^S(OEt)** in KBr disc (**a**) and in $CHCl_3$ (**b**)

B. Electronic spectra of **1**, $VOL_2^S(OEt)$ in $CHCl_3$

The precursor complex, **1** exhibits the usual spectral characteristics of a monoalkoxo-bound monooxo-vanadium(V) and μ-oxo-divanadium(V) complex in $CHCl_3$. Thus, the electronic spectral study also proves the generation of a divanadium(V) center when the complex is present in solution, $CHCl_3$. Spectra of the vanadium(V) exhibit (**Figure 4.5**) several absorption bands in the 300-500 nm region. The band near 400 nm is assigned to ligand to metal (LMCT) charge transfer transition, where as other higher energy bands are due to intraligand transitions [13, 23, 24, 25].

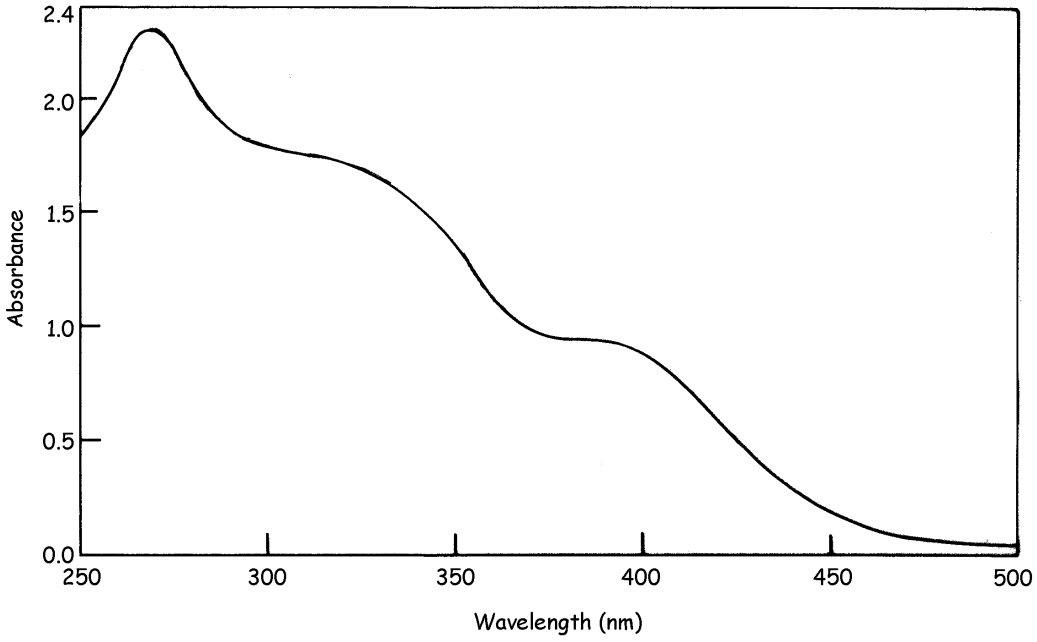


Figure 4.5 Electronic spectra of **1, VOL_2^S(OEt)** in $CHCl_3$

3.2. Redox Properties

The redox property of complex **1** has been examined in CH_3CN solution by cyclic voltammetry using a platinum working electrode, platinum counter electrode and a SCE reference electrode. The precursor compound $VOL_2^S(OEt)$ displayed a quasireversible cyclic voltammetric response near 0.45 V. This response is probably due to $(VOL^3)_2O$ / $[(VOL^3)_2O]^-$ couple [13, 25]. Because the monomeric complex gets converted to the dimer in CH_3CN solution.

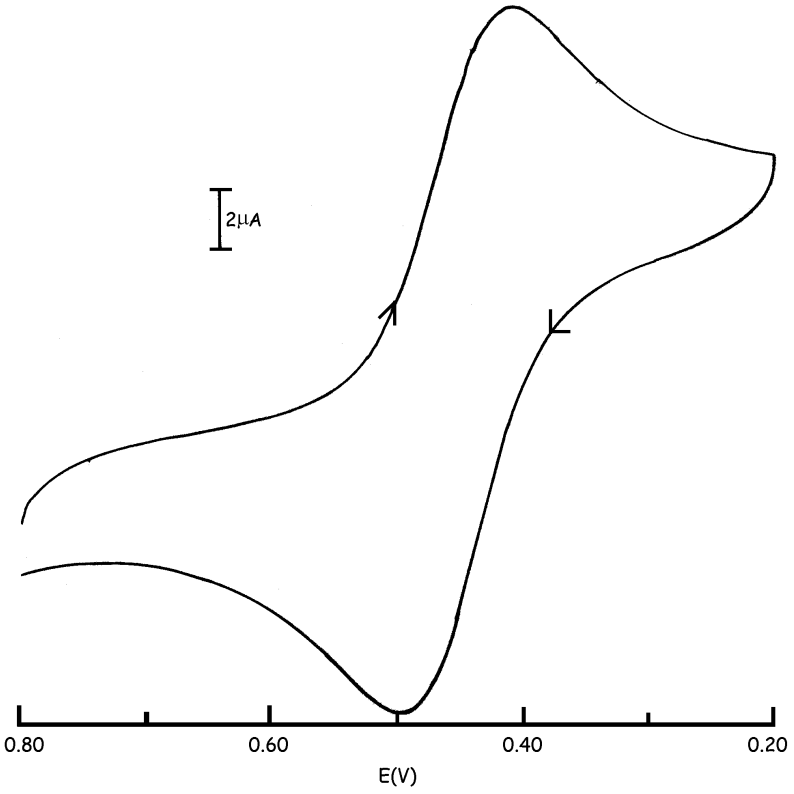


Figure 4.6 Cyclic voltammogram of **1, $VOL_2^S(OEt)$** in CH_3CN (0.1M TBAP) at a platinum electrode; scane rate 50 mV/s and potentials recorded vs SCE

2.4. Magnetic Study:

Since μ_{eff} value is negative, the metal complex **1** is diamagnetic indicating the presence of vanadium in the +V oxidation state. The magnetic moment is changing with a d^0 electronic configuration of **1** (μ_{eff} = - 7.65) showing the oxidation of +IV to +V state (**Method-1**). But in (**Method-2)** the magnetic moment is remains intact (both in d^0) in the starting precursor and in complex **1.**

2.5. Description of Structure of Complex 1:

The molecular structure of **1** is shown in **Figure 4.7** and important geometric parameters are listed in **Table 1.1**. The VO_4N coordination sphere around the mono alkoxo-bound monooxo-vanadium(V) is grossly square pyramidal. The basal plane is made up by the phenolic oxygen O(3), the enolic oxygen O(4), the imine nitrogen N(1) from the tridentate ligand and O(2) from the deprotonated alkoxide oxygen. The Schiff base ligand *2*-Hydroxyacetophenonehydrazone of 2-Hydroxybenzoylhydrazine Ligand ($L_2{}^SH_2$) forms a six-membered and a five membered chelate ring at the V(V) acceptor center. The apical position of square pyramid is occupied by the terminal oxo-group O(1). The short V(1)-O(1) distance of 1.5871(9)Å indicates the presence of a vanadium-oxygen double-bond (V = O) which is commonly found in five and six coordinated octahedral complexes [17,20,25] of vanadium(IV) and (V). The four V-O bond lengths are unequal; the V=O bond being the shortest and the V-O [enolate oxygen O(4)] being the longest. The latter is subjected to the trans influence of the oxo oxygen. The V-O bond lengths follow the

order V-O (oxo) < V-O (alkoxide) < V-O (phenoxide) < V-O (enolate). This data indicate stronger binding of the alkoxo group compared to those of phenoxo and enolate oxygen atoms.

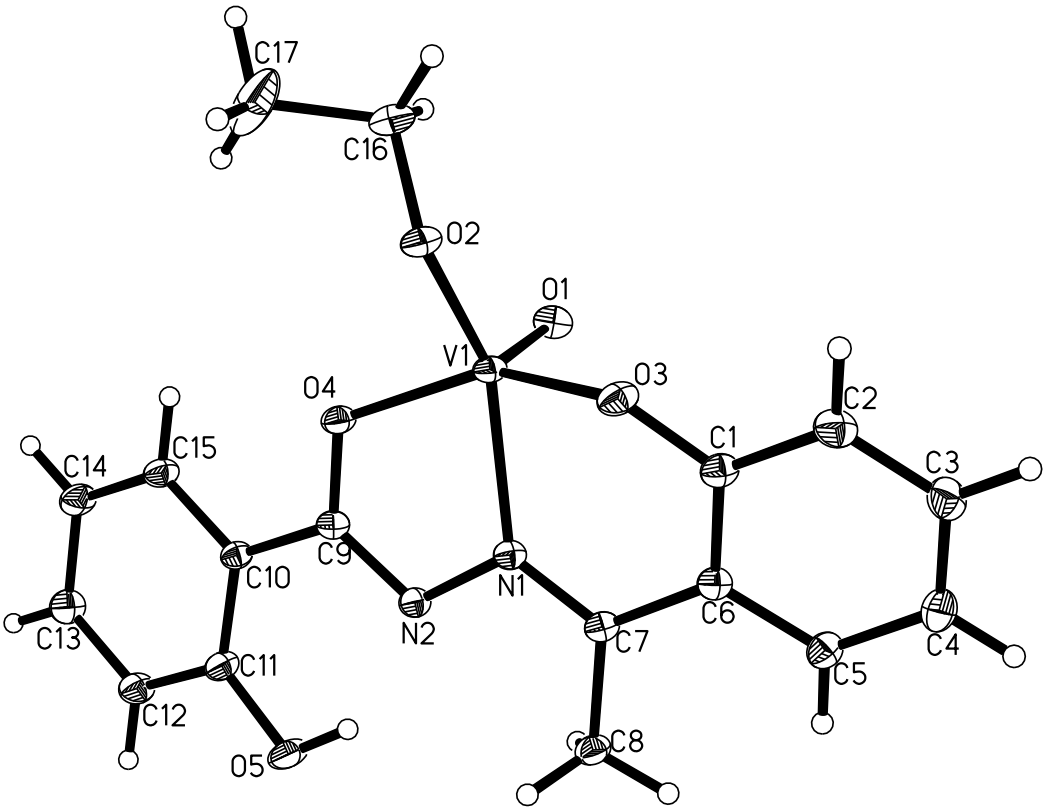


Figure 4.7 ORTEP plot of **1, VOL_2^S(OEt)**

Table 1.1 Selected bond Distances (Å) and bond angles (deg) for **Complex 1**

	Distances		
V(1) – O(1)	1.5871(9)	V(1) – O(4)	1.9462(9)
V(1) – O(2)	1.7440(9)	V(1) – N(1)	2.1254(10)
V(1) – O(3)	1.8228(9)	C(11) – O(5)	1.3557(14)
	Angles		
O(1) – V(1) – O(2)	106.80(4)	O(1) – V(1) – N(1)	98.48(4)
O(1) – V(1) – O(3)	104.13(5)	O(2) – V(1) – N(1)	153.30(4)
O(2) – V(1) – O(3)	99.50(4)	O(3) – V(1) – N(1)	82.15(4)
O(1) – V(1) – O(4)	101.75(4)	O(4) – V(1) – N(1)	75.02(4)
O(2) – V(1) – O(4)	91.27(4)	O(3) – V(1) – O(4)	147.60(4)

In the three dimensional extended structure of **1,** there is a notable feature of the crystal structure is that, the phenolic hydrogen atom of the hydrazide part of the ligand participates in intramolecular hydrogen bond with the imine nitrogen atom N(2) to form a pseudo five-membered ring **Figure 4.8.** Besides a set of complementary H-bonding between the phenolic OH (hydrazide) of one moiety with the deprotonated –OH from the carbonyl part of the ligand from another molecule forms an H-bonded dimmer.

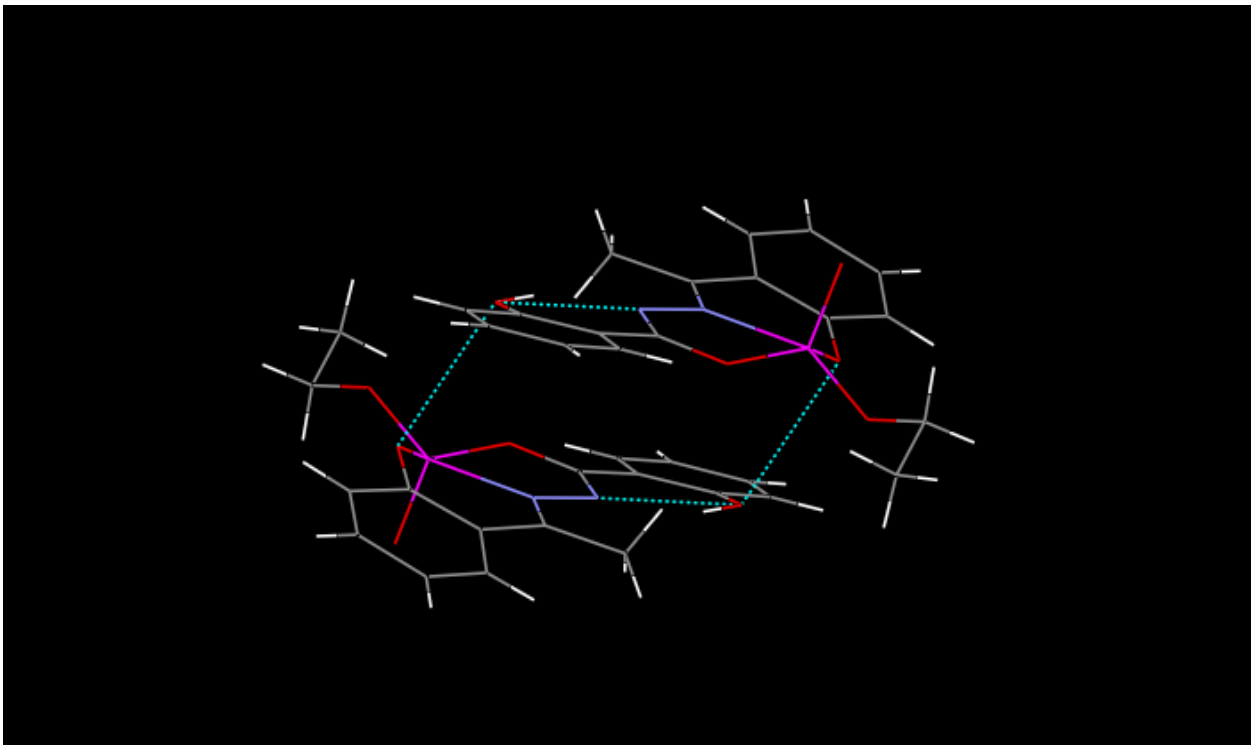


Figure 4.8 Three dimensional extended structure of **1, VOL_2^S(OEt)**

The packing diagram **Figure 4.9** of complex **1** exhibits a intramolecular hydrogen bond between the imine nitrogen atom N(2) and the phenolic hydrogen atom of the hydrazide part of the ligand along *b* axis. Each cube can contain six metal complexes along *b* axis. There is also an intermolecular hydrogen bond between the phenolic OH (hydrazide) of one moiety with the deprotonated –OH from the carbonyl part of the ligand from another moiety.

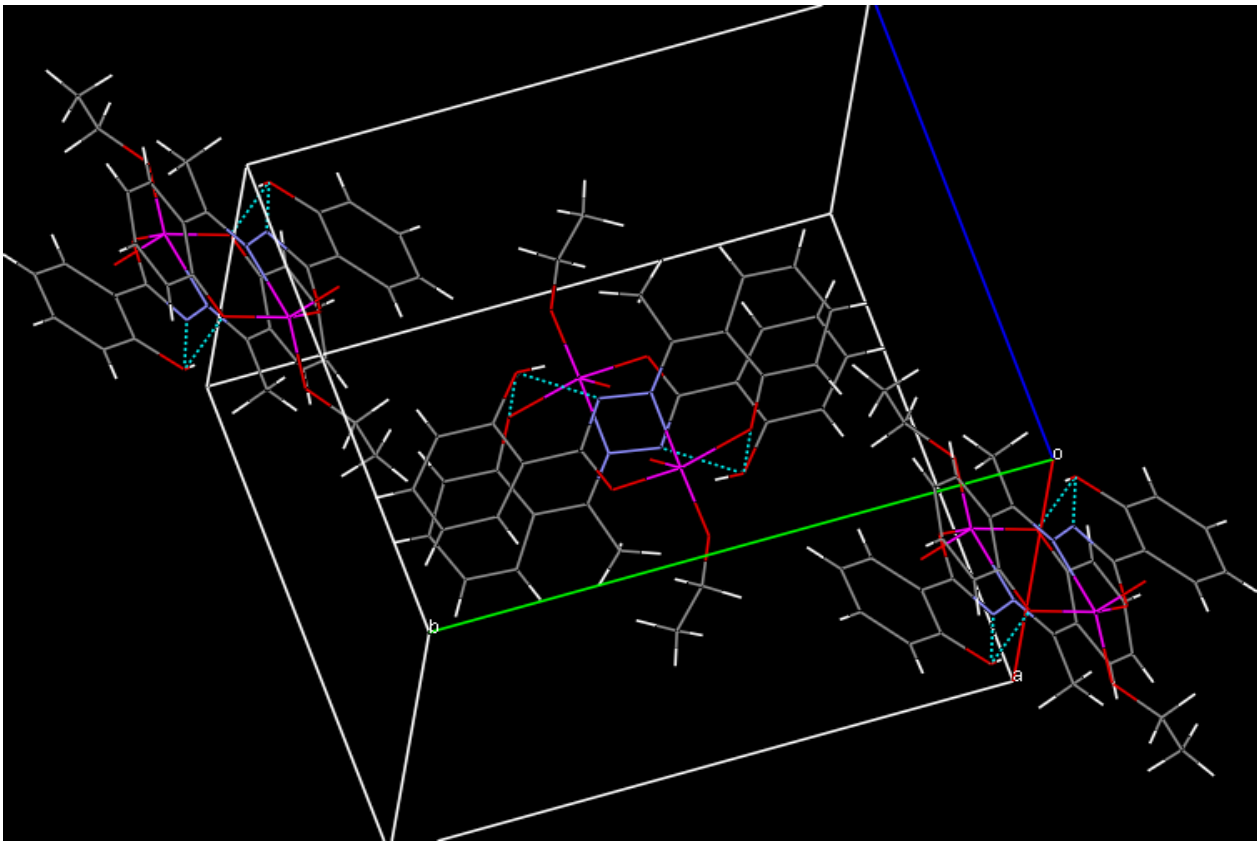


Figure 4.9 Packing diagram of complex **1, $VOL_2^S(OEt)$** along *b* axis

Table 1.2 Crystal data and details of refinement for the complex $VOL_2^S(OEt)$ (**1**)

Chem formula	$C_{17}H_{17}N_2O_5V$
Fw	380.27
Cryst syst.	Monoclinic
Space group	$P2_1/c$
a, Å	9.4572(6)
b, Å	15.1434(8)
c, Å	12.1202(7)
V, *Å*^{3}	1637.44(16)
Z	4
T, K	100(2)
λ, Å	0.71073
D_c, Mg m^{-3}	1.543
μ (Mo Kα) mm^{-1}	0.637
F (000)	784
R1, wR2 [$I > 2\sigma(I)$]	0.0317, 0.0830
Goodness of fit on F^2	1.060

3. CONCLUSION:

Several Schiff's base hydrazone ligands were synthesized and successfully characterized by IR and elemental (C, H, N) analyzer. The basic and electronic property of these ligands has been nicely explored in the syntheses of various oxovanadium(V) complexes. One (complex **1**) of the five complexes reported here, has been fully characterized by IR, UV-visible spectroscopy, magnetic susceptibility, cyclic voltammetry measurement, and structurally characterized by single crystal X-Ray crystallography. This study indicates that the lower basic hydrazone ligands (e.g., $L_2{}^SH_2$) have the normal tendency to form monomeric complexes. I also have reported the synthesis of few other oxovanadium complexes (**2-4**) but due to insufficient data and shortage of time we are unable to report the complete characterization of all those complexes.

STUDIES UNDER PROCESS:

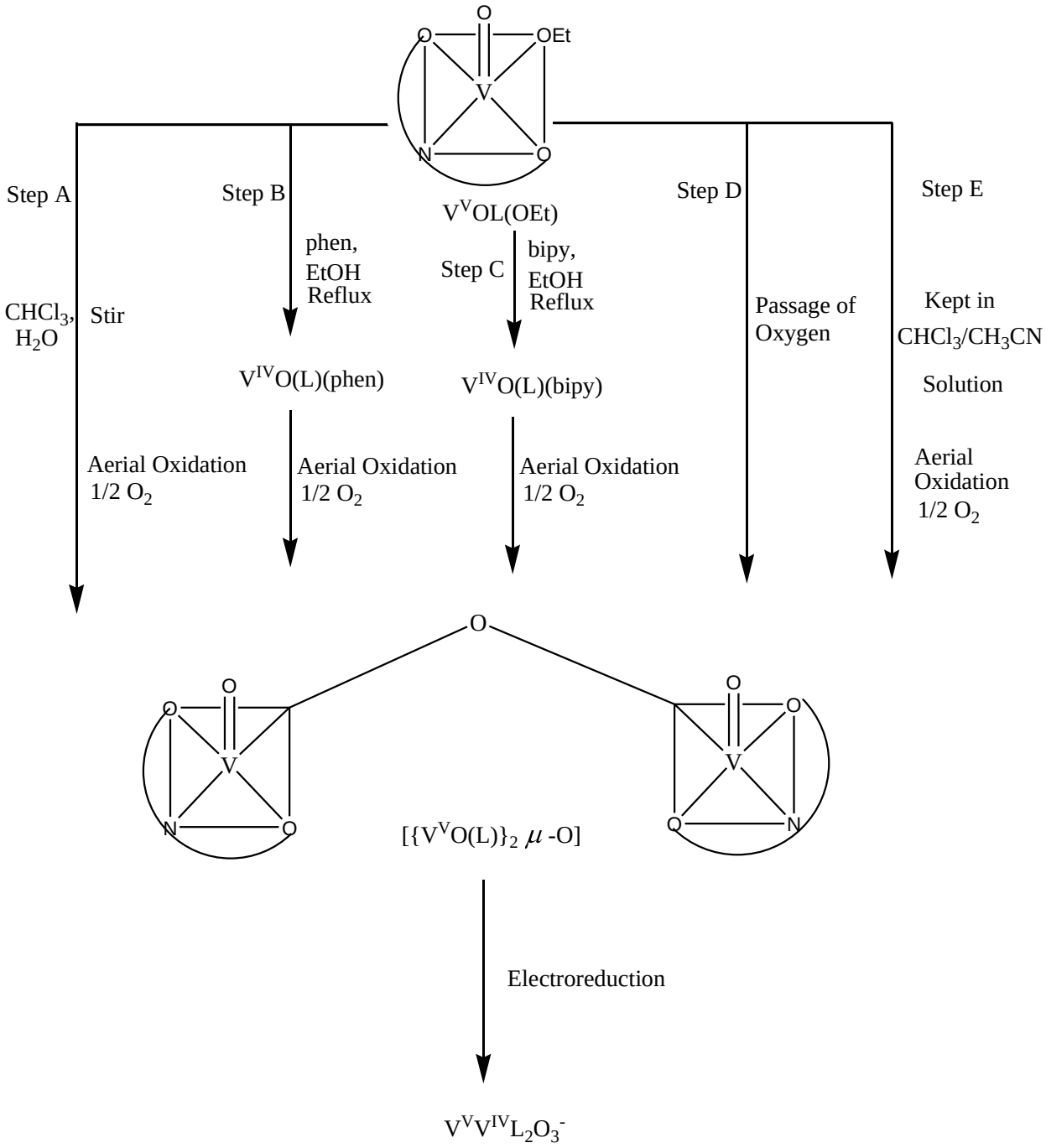
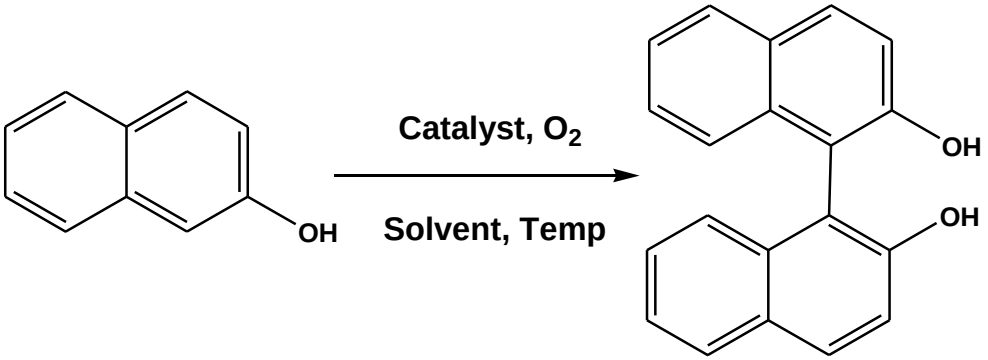
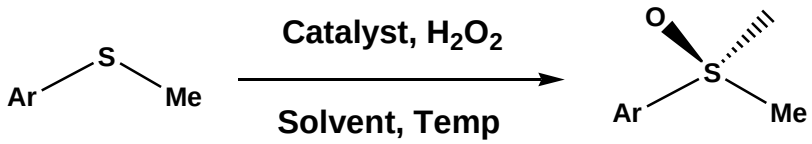


Figure 5.1 Reaction diagram for the isolation of divanadium(V) from vanadium (V),and mixed valence V(IV,V) complex

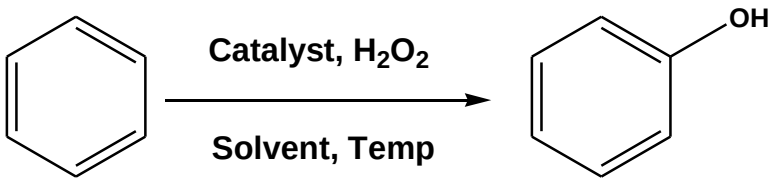
FUTURE STUDIES:



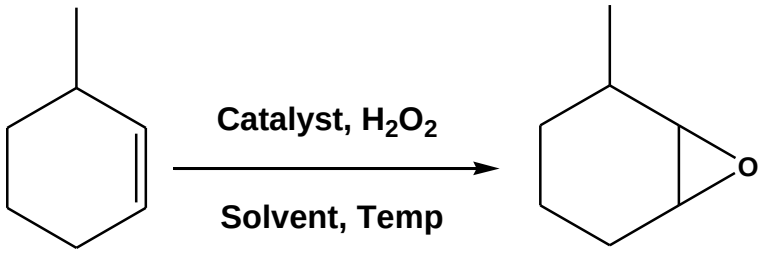
Scheme- 1: Oxidative coupling of 2-Napthol



Scheme- 2: Enantioselective Oxidation of Sulfides



Scheme- 3: Hydroxylation of Arene with peroxide



Scheme- 4: Selective epoxidation of alkenes

Figure 5.2 Few examples of proposed study of catalytic activity using variable-valence mono- and binuclear oxovanadium complexes

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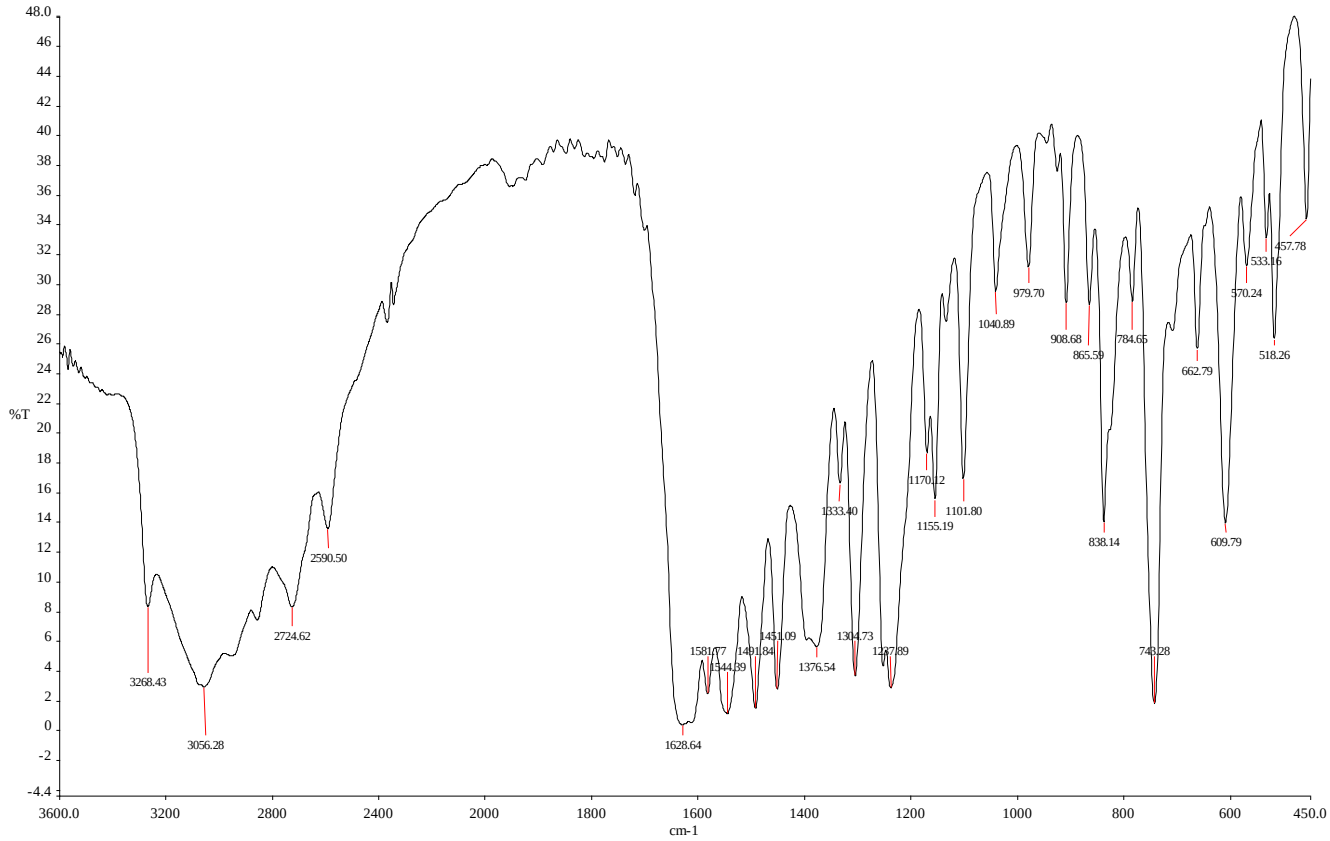
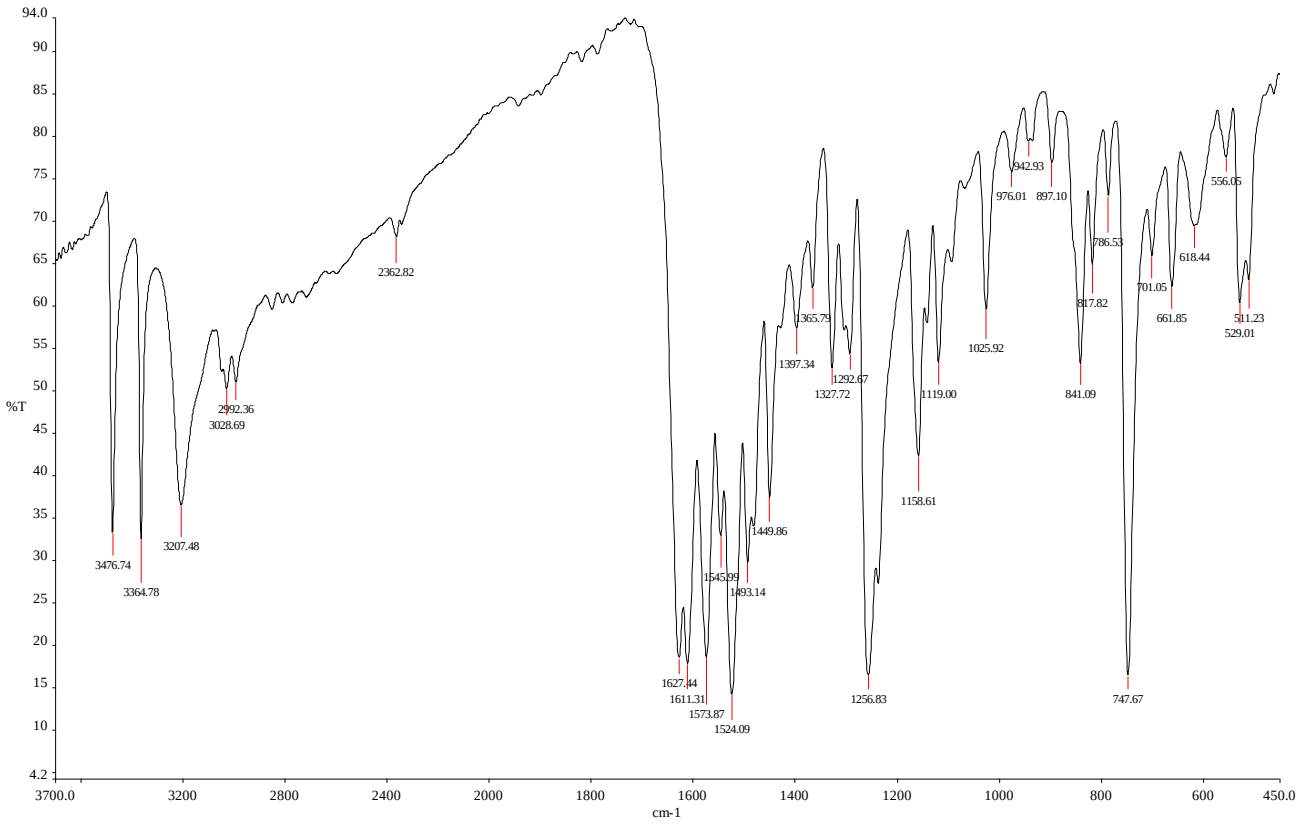
SPECTRAL DATA



IR Spectral Data of $L_2{}^{S}H_2$



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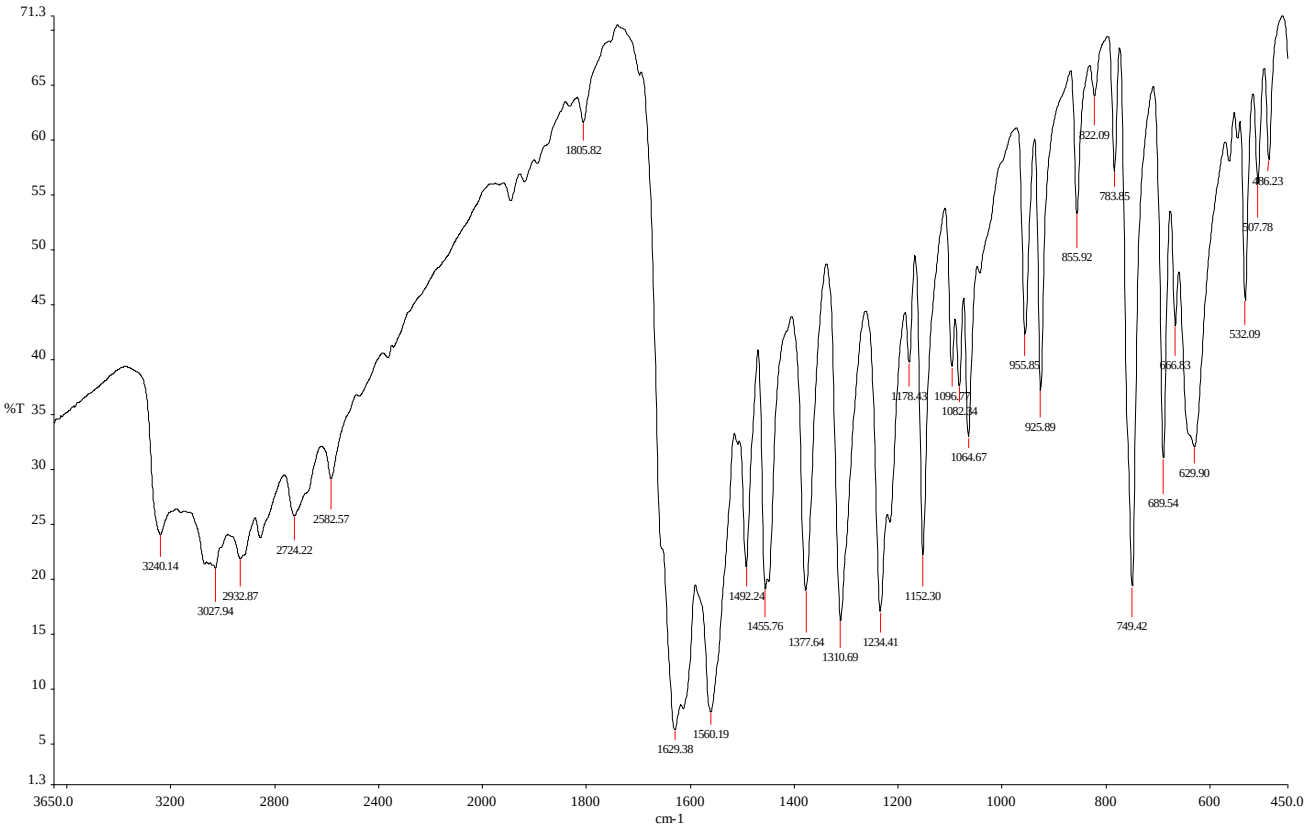

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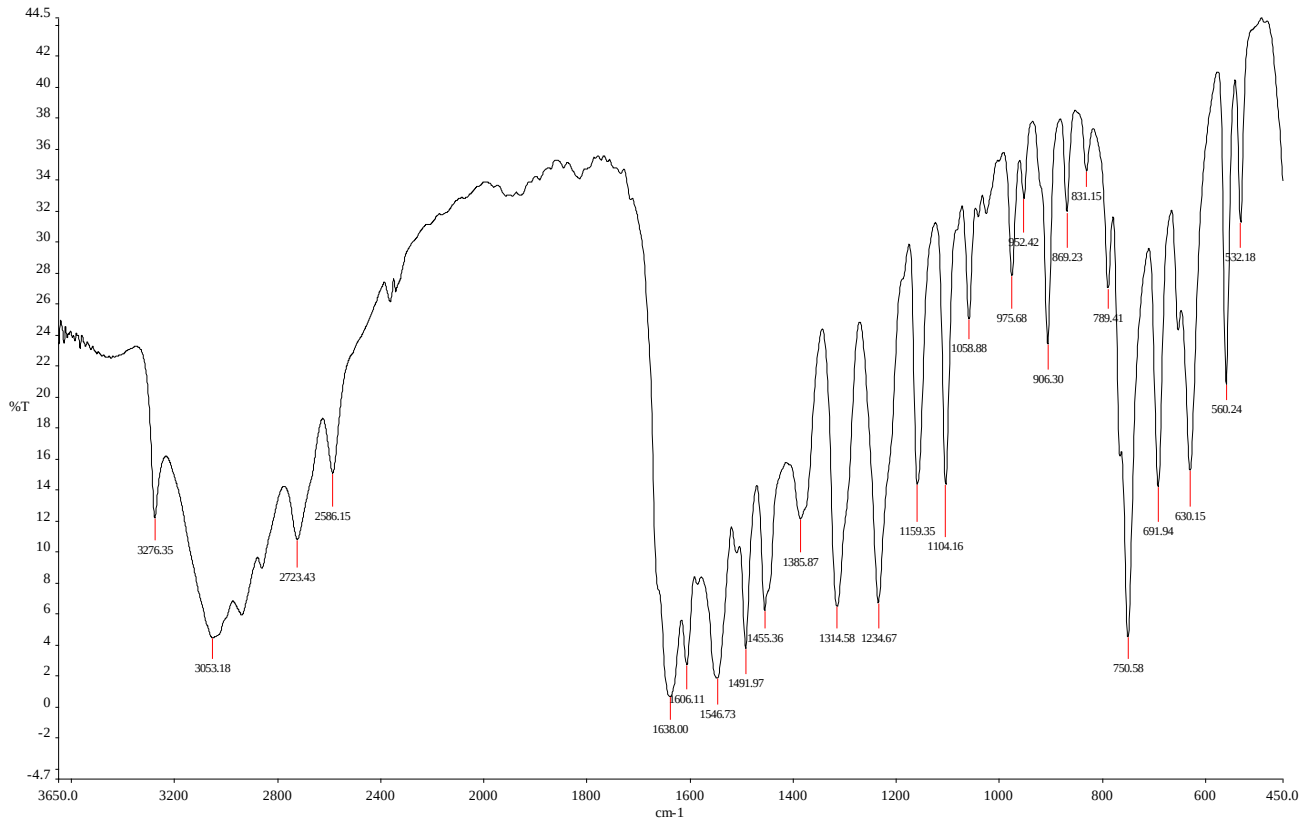

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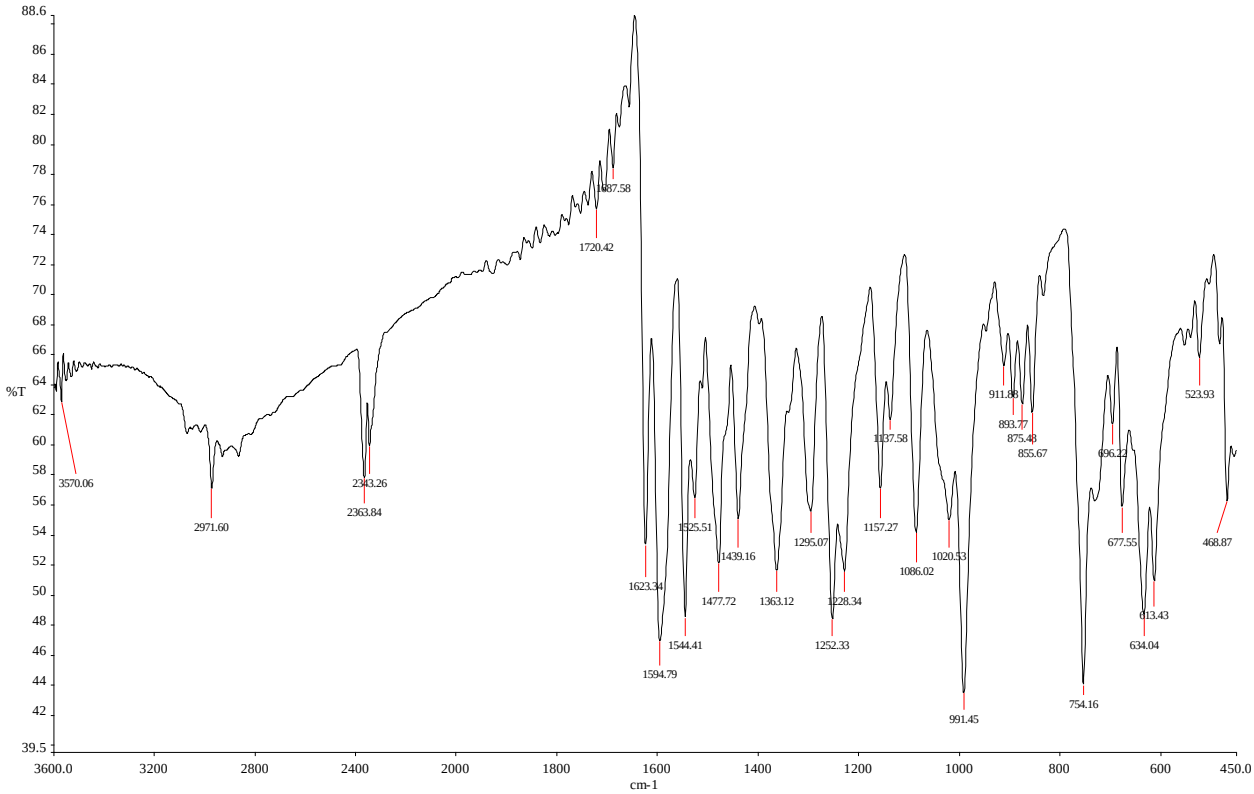
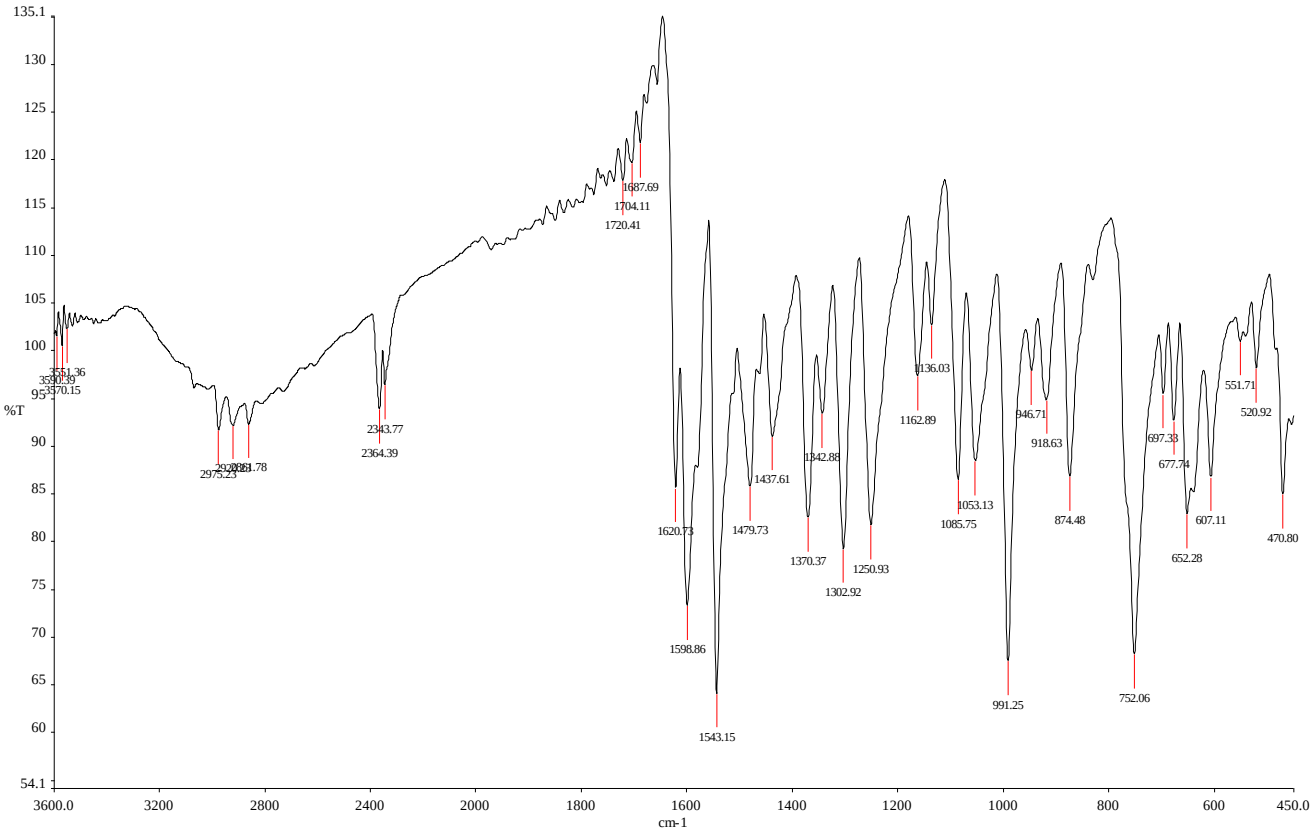
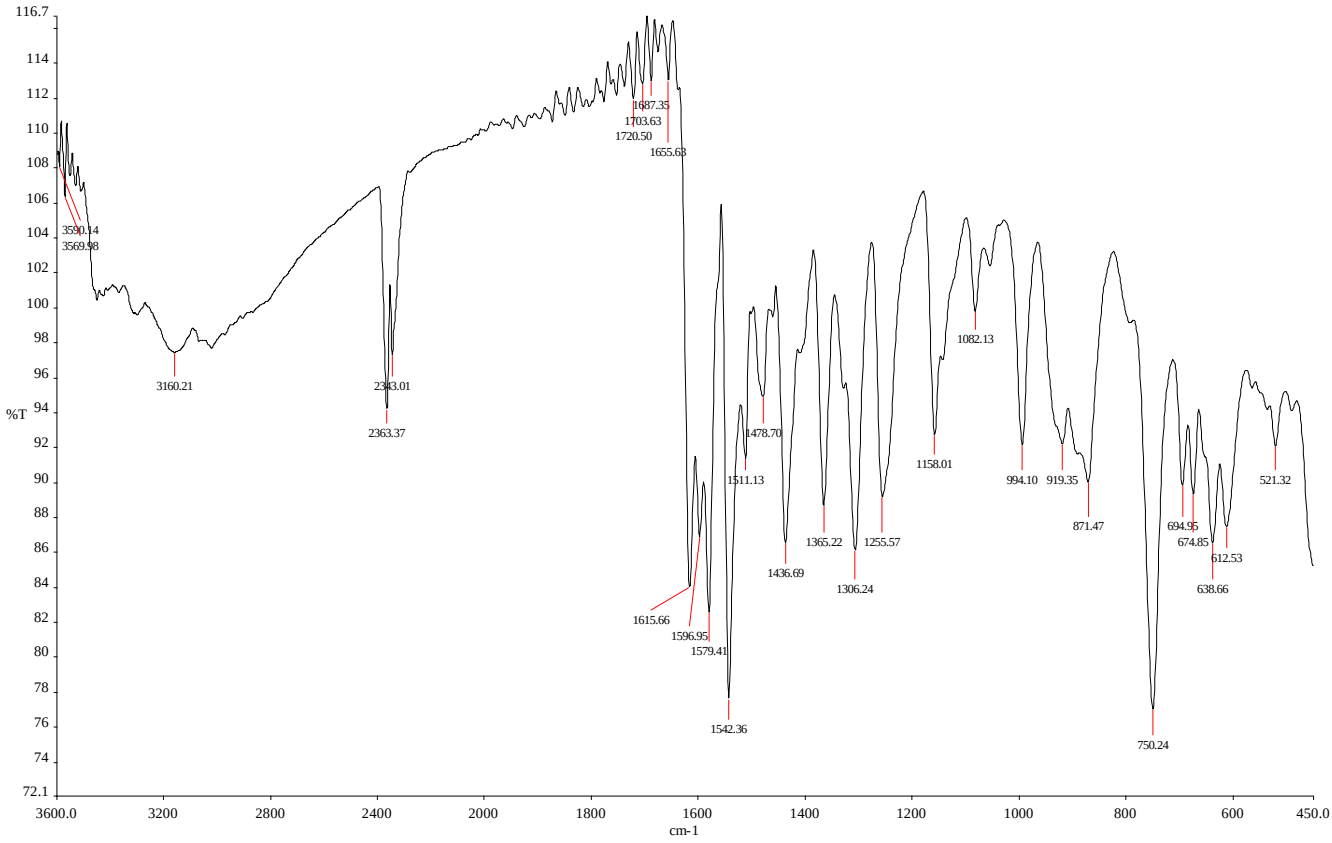


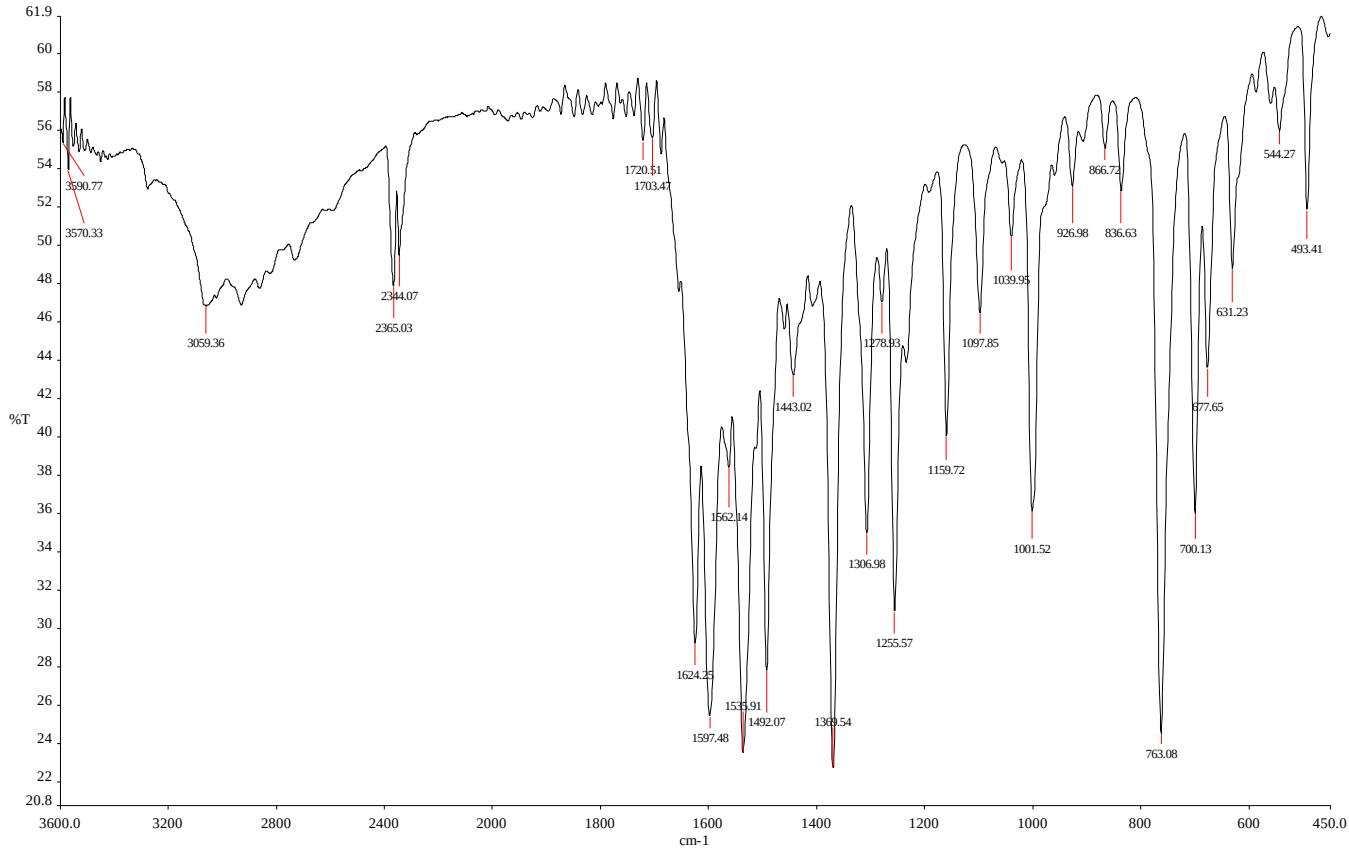
IR Spectral Data of **Complex-1, [$V^{V}OL_2^{S}(OEt)$]** (Method-1)



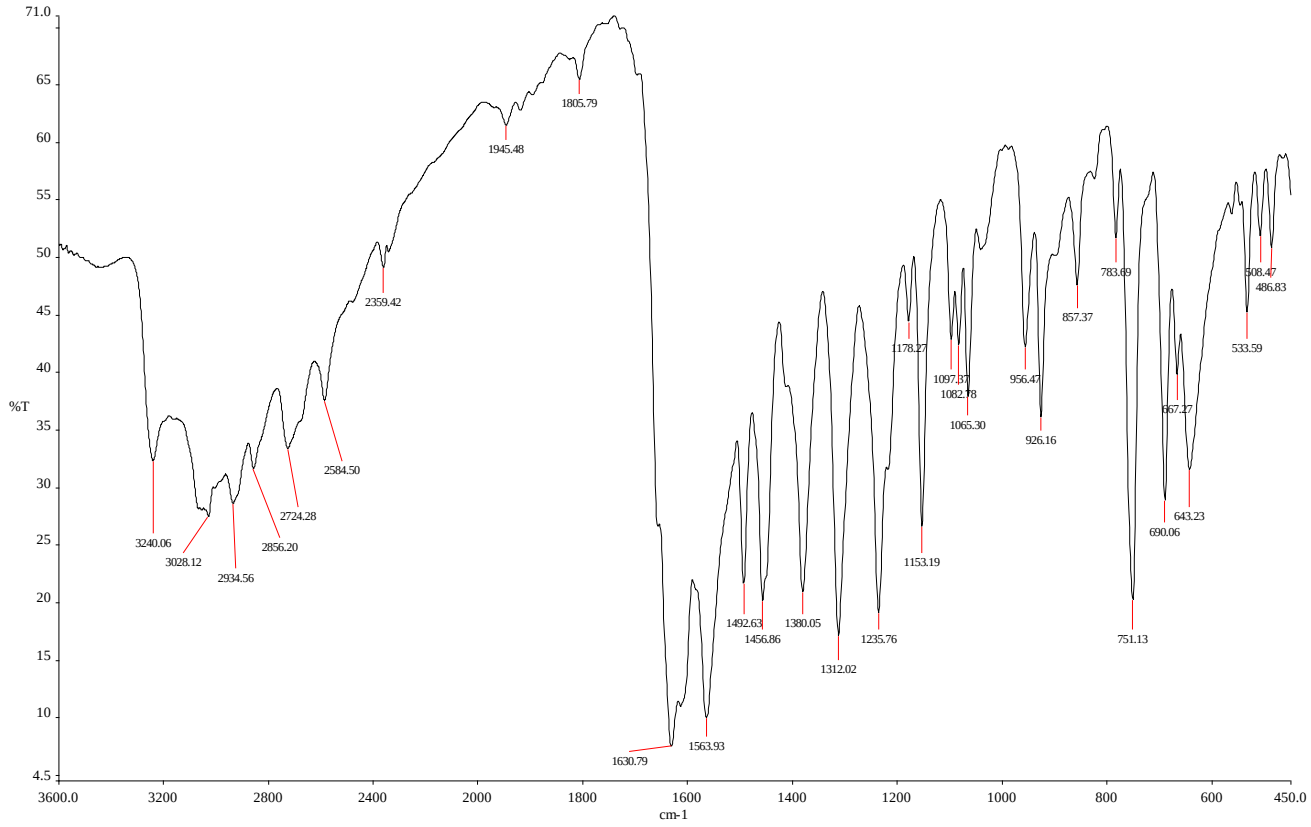
IR Spectral Data of **Complex-1, [$V^{V}OL_2{}^{S}(OEt)$]** (Method-2)



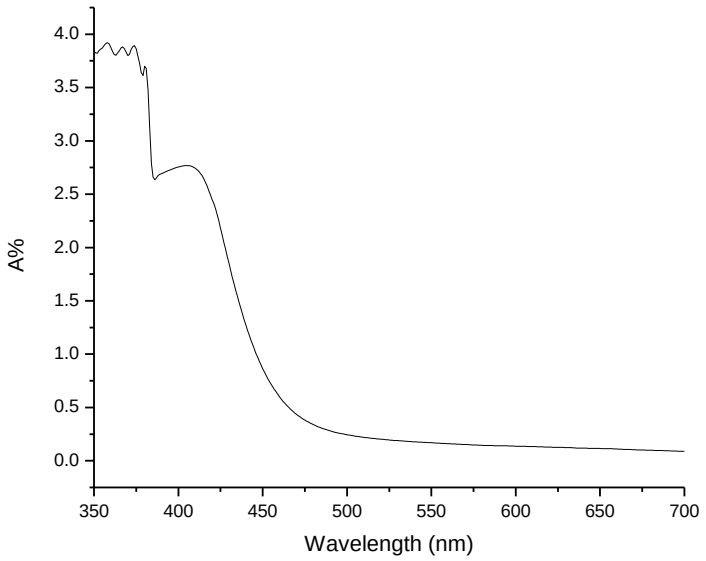
IR Spectral Data of **Complex-2, $[V^{V}OL_2^{A}(OEt)]$**



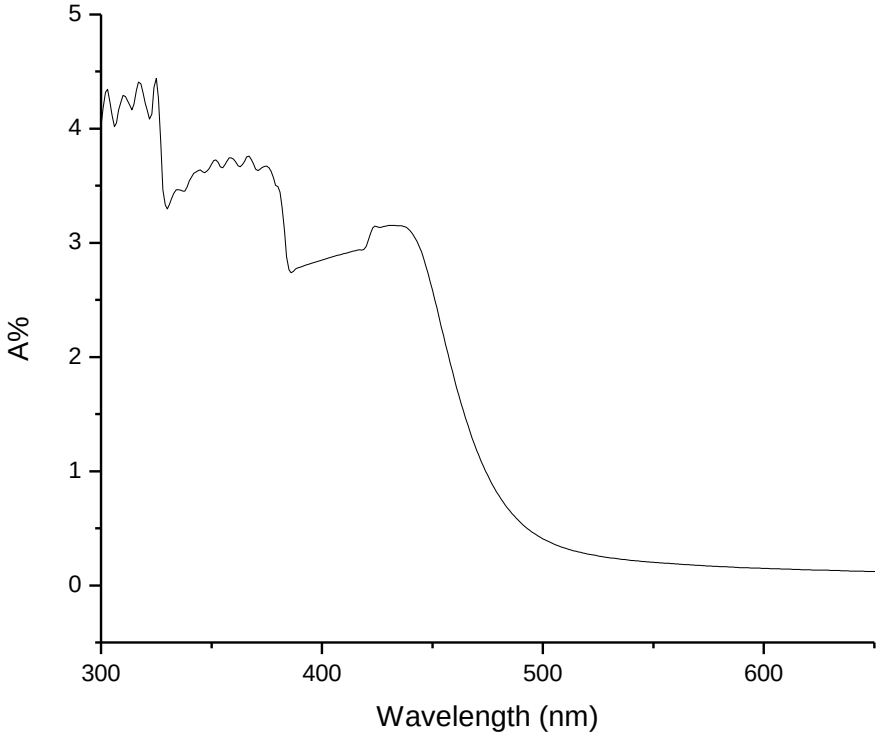
IR Spectral Data of **Complex-3, $[V^{V}O(L_2{}^{S})_2(OEt)]$**



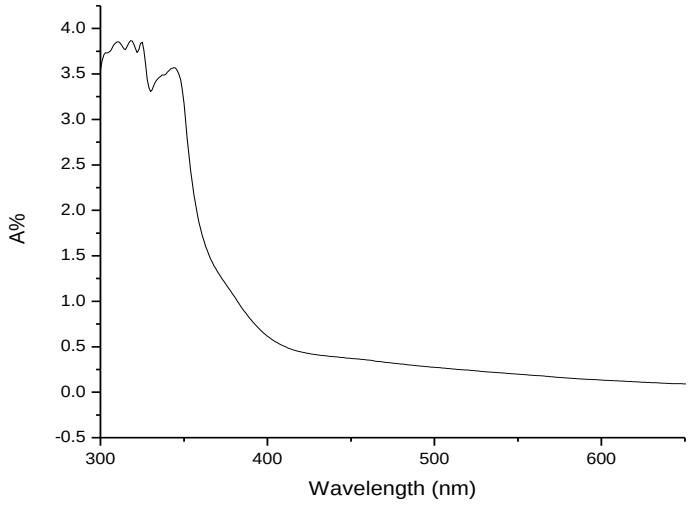
IR Spectral Data of **Complex-4, $[V^{V}O(L_1{}^{S})_3]$**



Electronic spectra of **1,** $V^{V}L_2{}^{S}(OEt)$ in $CHCl_3$



Electronic spectra of **2,** $V^{V}OL_2{}^{A}(OEt)$ in $CHCl_3$



Electronic spectra of **4**, $V^{V}O(L_1{}^{S})_3$ in $CHCl_3$